



## Synthesis of a thermosensitive surface by construction of a thin layer of poly(*N*-isopropylacrylamide) on maleimide-immobilized polypropylene

Thelma S.P. Cellet<sup>a</sup>, Marcos R. Guilherme<sup>a</sup>, Rafael Silva<sup>b</sup>, Guilherme M. Pereira<sup>a</sup>, Marcos R. Mauricio<sup>a</sup>, Edvani C. Muniz<sup>a</sup>, Adley F. Rubira<sup>a,\*</sup>

<sup>a</sup> Grupo de Materiais Poliméricos e Compósitos, Departamento de Química, Universidade Estadual de Maringá, Av. Colombo, CEP 87020-900 Maringá, PR, Brazil

<sup>b</sup> Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854, USA

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### ABSTRACT

Thermosensitive surfaces were developed by the grafting of a thin layer of PNIPAAm through an UV-induced photopolymerization reaction of vinyl monomers with a free radical-activated polypropylene (PP) surface. PNIPAAm layer covering the PP surface corrected, to some extension, both depressions and fissures of the previously modified PP surfaces. The layered surfaces have morphological characteristics different from those of the non-layered surfaces, and their thickness was dependent on irradiation time. Water contact angles of the layered surfaces revealed a transition at approximately 33.5–36.5 °C as a result of a response to the variation of temperature. There was an increase in the values of the contact angles with an increase in temperature from 26 °C to 44 °C, revealing the nature both hydrophilic and hydrophobic of the surfaces due to a conformational rearrangement of PNIPAAm exposing its isopropyl groups to the liquid drop. This work offers a chemically stable thermosensitive surface (because it is covalently structured) with great potential for use as sensors and actuators.

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### 1. Introduction

The performance of polymer-based materials for both traditional and modern applications depends not only on structure-related properties, such as malleability, thermal stability, mechanic resistance, but also on their surface properties and interface behavior. Applications in which the surface properties play a protagonist role, such as wettability, adhesion, adsorption, lubrication, biocompatibility, and permeability [1–5], depend substantially on chemical nature of the polymer device. Chemical modification of a polymer surface is an interesting strategy to extend the use of devices that exhibit both properties and structures of well-defined volume. There are many methodologies that have been developed over last decades with the purpose of producing devices that exhibit specified surface properties [6–12]. Physical methods, such as plasma modification, ultraviolet irradiation, and corona discharge, can be used to modify the surface properties of polymers [13–15]. These methods are excellent tools to produce functionalized surfaces with a high covering degree but they require specific operating conditions, such as high energy discharge, ambient with controlled atmosphere and low pressure. The chemical modification of inert surfaces can also be performed by both the functionalization of the polymer surface with the use of oxidizing agents

in aqueous solution or gas phase and the grafting of molecules with a specific activity [13–17]. Usually the functionalization is enough to produce surfaces with specific characteristics. However, in some cases, it is the initial step of the modification process that is followed by the grafting. Modification based on production and on immobilization of macromolecules is also a useful and interesting way to activate surface of polymers. Polypropylene (PP) is a thermoplastic polymer of hydrophobic nature with inert surface. Furthermore, it is insoluble at room temperature even in organic solvents, and complete solubility is possible only at high temperatures in some organic solvents. PP possesses interesting properties, such as mechanical resistance, flexibility, low specific weight, thermostability, and good transparency [18–20], which make it an important device for uses in biotechnology, and is cheap to purchase. Furthermore, PP is also appropriate for *in vivo* tests because it neither produces nor releases fragments of toxic substances in a biological environment. In biotechnology, poly(*N*-isopropylacrylamide) (PNIPAAm) has been of great interest because of a transition from a hydrophilic to hydrophobic macromolecule as the temperature is raised above 30–35 °C. In water, it exhibits reversible phase transition at lower critical solution temperature (LCST) with resulting dramatic shrinkage [21–24]. Furthermore, PNIPAAm has been used in controlled drug release, and cell culture [25,26]. The grafting of PNIPAAm on the PP surface to produce smart materials means that this device would have somewhat impact on biotechnology. The grafting of PNIPAAm layer on surfaces has been

\* Corresponding author. Fax: +55 44 3011 4125.

E-mail address: afrubira@uem.br (A.F. Rubira).

described in the literature [27,28]. In this work, our attention has been focused on developing temperature-sensitivity surfaces by the grafting of a thin layer of PNIPAAm on PP with a free radical-activated surface. This type of device has not been reported yet and can be recognized as a smart material in terms of state-of-the-art applications as sensors and actuators. The process consists of anchoring free functional groups on PP, creating a free radical-activated (functionalized) surface, for a further UV-induced photopolymerization reaction of vinyl monomers through a five-step surfacing technique: (1) modification of PP with maleic anhydride (APP), (2) amination of maleic anhydride-modified PP ( $\text{NH}_2\text{APP}$ ), (3) reaction of maleic anhydride with  $\text{NH}_2$ /anhydride-modified PP (ANHAPP), (4) cyclization reaction for immobilizing maleimide on anhydride/ $\text{NH}_2$ /anhydride-modified PP (MALPP), and (5) UV-induced polymerization reaction of NIPAAm with the maleimide immobilized on PP (PNIPAAm-g-MALPP). This work proposes a chemically stable thermosensitive surface (because it is covalently structured) with great potential for use as sensors and actuators.

## 2. Materials and methods

### 2.1. Materials

Polypropylene (Aldrich, isotactic, average  $M_w \sim 50,000 \text{ g mol}^{-1}$ , melting point 160–165 °C, density  $0.9 \text{ g mL}^{-1}$  at 25 °C), acetic anhydride (Aldrich,  $\geq 99\%$ ), maleic anhydride (Aldrich,  $\geq 99\%$ ), ethylenediamine (Aldrich,  $\geq 99\%$ ), acetone (F. Maia,  $\geq 99.5\%$ ), chloroform (Synth,  $\geq 99.8\%$ ), sodium acetate anhydrous (Nuclear,  $\geq 99\%$ ), *N*-isopropylacrylamide, NIPAAm, (Acros Organics  $\geq 98\%$ ). The analytical grade reagents, except NIPAAm, were used without further purification.

### 2.2. PP processing

Isotactic PP surfaces were prepared from PP-based pellets using a 4 cm-length, 3 cm-width dimension rectangular plate in a mechanical heat press. The samples were submitted to pressure of 30.1 MPa at 165 °C for 3 min and subsequently cooled in an ice bath. Surface-cleaning process was performed in a glass balloon-fitted Soxhlet extractor by passing acetone through the samples for 24 h.

### 2.3. Synthesis and immobilization of maleimide on the PP surface for photopolymerization

#### 2.3.1. Grafting reaction of maleic anhydride on the PP surface (APP)

PP samples were immersed into a solution consisting of 80 mL acetic anhydride and 4 g maleic anhydride at temperature of 100 °C under strong stirring. After that, 0.44 g of benzoyl peroxide was introduced to mixture that was kept under stirring for 6 h. After being taken from solution, the samples were washed with acetone (three times, 500 mL each) in order to remove the maleic anhydride in excess and subsequently washed with water by Soxhlet extraction for 24 h.

#### 2.3.2. Amination of the APP surface with ethylenediamine ( $\text{NH}_2\text{APP}$ )

APP samples were immersed into 50 mL of ethylenediamine for 5 h at 100 °C. After that, the samples were taken from the liquid and washed with acetone by Soxhlet extraction for 24 h.

#### 2.3.3. Treatment of the $\text{NH}_2\text{APP}$ surface with maleic anhydride (ANHAPP)

$\text{NH}_2\text{APP}$  samples were immersed into a solution consisting of 2 g maleic anhydride and 30 mL chloroform. The resulting solution

was kept under reflux for 24 h, and subsequently the samples were taken to be washed with water in the Soxhlet extractor for 24 h.

#### 2.3.4. Cyclization reaction for immobilizing maleimide on the ANHAPP surface (MALPP)

ANHAPP samples were immersed into 30 mL of acetic anhydride containing 0.1 g of sodium acetate anhydrous at 60 °C for 24 h. Later, the resulting samples were washed with water in the Soxhlet extractor for 48 h.

#### 2.3.5. UV-induced polymerization reaction of NIPAAm with MALPP (PNIPAAm-g-MALPP)

MALPP samples were introduced into a 1.0 mm-internal diameter quartz cuvette that was filled up with aqueous-NIPAAm solution of  $1.40 \text{ mol L}^{-1}$  concentration. The mixture-containing cuvette was exposed to the UV irradiation of a low-pressure Hg vapor lamp 250 W at different photopolymerization times. The distance from the lamp to the cuvette was 30 cm. Thereafter, resulting products were washed with water by dispersion in an ultrasonic bath 1440 A (Ondontobrás) by applying a frequency of 44 kHz. Subsequently the products were washed with water in the Soxhlet extractor for 48 h in order to remove unreacted NIPAAm or any other residues that could be only physically sorbed on the samples.

#### 2.3.6. Characterization studies of the final and intermediate products

Chemical characterization of the products was performed by attenuated total reflection in Fourier Transform Infrared (ATR-FTIR) using Bomem model MB-100 equipped with a Pike MIRacle ATR accessory at an incident angle of 45° and a ZnSe crystal under nitrogen stream. Atomic force microscopy (AFM) images and values of roughness mean square (RMS) of the surfaces were obtained in Shimadzu SPM-9500J3. Morphological characterization was performed in a scanning electron microscope (Shimadzu, model SS 550 Superscan). SEM images were made applying an accelerating voltage 15 kV and a current intensity of 30 mA.

Thermosensitive properties of the layered surfaces were evaluated by static contact angle variations of water drops on the surfaces of films as a function of temperature using a contact angle meter (Tantec, Model Cam-Micro) with a controlled-temperature metal cell having a 5-cm<sup>2</sup> smooth surface on which the films were carefully fixed, and equilibrated at 25 °C for 5 min. The contact angle measurements of the surfaces layered at different polymerization times were performed at temperatures of 26 °C, 28 °C, 30 °C, 32 °C, 34 °C, 36 °C, 38 °C, 40 °C, 42 °C and 44 °C. Data of contact angles were calculated as the average over four points on the surface of three different samples, totalizing twelve determinations per film.

## 3. Results and discussion

Maleimides are a special class of vinyl compounds with a strong electron-acceptor characteristic due to its chemical structure that has two carbonyl groups bonded to a vinyl group ( $>\text{C}=\text{C}<$ ) [29–31]. Vinyl group of the maleimide undergoes electronic transition to an excited state when exposed to UV irradiation at a specific wavelength. It is important to report that the hydrogen-donating groups in its structure are essential to start off polymerization through radical ions resultant from proton–electron transferences [32]. A simple photopolymerization reaction of NIPAAm with MALPP is demonstrated in Fig. 1. After the UV light exposition, there is the formation of a radical ion on the vinyl group of the maleimide that attacks the carbon–carbon  $\pi$ -bonds of NIPAAm, and thus the photopolymerization process starts off with the addition of new NIPAAm radicals to the ever-increasing chain. It is important to

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