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Thermosensitive poly(N-vinylcaprolactam) as a transmission light regulator in smart windows

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ABSTRACT

Upcoming generation of smart windows requires simple design, fast stimulus response and cost-effective production. Aiming these features, we reported a new approach of switchable devices based on the thermosensitive polymer poly(N-vinylcaprolactam) (PNVCL) and facile assembly of the components (FTO layers and polymer). Its optical/color change from transparent to opaque is temperature-dependent and activated by induced Joule heating of conductive substrates. Therefore, the reported devices showed fast reversible response (less than 60 s) by small input power and adjustable opaqueness according to polymer concentration. In opposite to traditional electrochromic smart windows dependence of the kinetics charge-transfer reaction, the observed features are triggered by the thermodynamic mechanism of the reversible coil-globule transition from PNVCL suspension, which can lead to stable performance of the proposed device.

1. Introduction

Smart windows (SW) are one of the most promising green technologies for energy harvesting, which next generation breakthrough relies on climate adaptive buildings by the regulation of solar energy transmission. These devices are designed to reduce air conditioning costs through sunlight blocking in summer and improve light harvesting during winter. Their fundamental mechanism is based on the tunable optical transmittance of incorporated switchable devices, generally promoted as a response of an applied bias or changes in environmental conditions [1].

Traditionally, switchable devices employ electrochromic materials based on transition metal oxides, suspended particles or polymers dispersed in liquid crystals as active materials [2,3]. These SW are composed of multilayers of components, which color modulation is commonly achieved by oxidation/reduction processes and diffusion of ions activated by an external stimulus [4]. Then, some features as fast coloration/bleaching response to external voltage [5] and glare control can be obtained for electrochromic SW [6]. However, this type of device can be costly, require demanding steps for materials development and multilayers construction, which can also lead to reduced visible transmittance and limited modulation level [7–9]. Additionally, since they change their optical properties by switching between oxidized and reduced form [4], these electrochemical reactions can have a reduced performance overtime due to unwanted side reactions between the electrolyte and active materials [10], as decomposition of electrolytes and efficiency reduction of charge transfer reaction between the electrolyte and active materials [11,12].

Another class of switchable devices is based on thermotropic materials as polymer blends [13], hydrogels [14,15], block copolymers [16] and core/shell structures [17–20], being also reported in the patent literature [18]. They present a temperature-induced switching behavior caused by phase transition or separation process, or even differences in refractive indices of SW components. When the switching threshold is reached by the increase of temperature, the thermotropic material undergoes a phase transition, forming scattering domains with dimensions comparable to the wavelength of the solar spectral range that reflect the incident solar radiation [18,19,21]. Some features found for these switchable devices are low cost of products, passively switching mechanism with solar heat, and diversity of smart windows size and shape [18].

Among these thermotropic materials, thermosensitive polymers have the ability to fine-tune their transparency in response to surrounding conditions, inasmuch as they are structure/color-sensitive to temperature [14,19] and exhibit a cloud point in water or other solvents [21]. Thermosensitive polymers have been synthesized based on many formulations of synthetic and natural hydrogels [21], which features are highlighted in many biological applications, such as drug delivery, biosensors [22], tissue engineering and biotechnology [21]. On the other hand, the application of these materials as stimuli-

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sensitive materials in light-shielding switchable devices still remains little explored. The principle of thermosensitive polymers in switchable devices is their coil-globule transition in aqueous solution at specific temperature, called lower critical solution temperature (LCST), induced by solar energy or sensing environmental temperature changes [23]. Below this temperature, polymer chains are soluble in water by predominant hydrophilic forces and the medium is transparent [24,25]. However, when the system is heated above the LCST, intra- and inter-polymer interactions predominate, resulting in a homogeneous opaque agglomerate state promoted by hydrophobic interactions. The great advantage of employing this class of thermosensitive polymers in SW is the longtime stability assured by entropic effect, high transparency in the clear state with low haze, outstanding switching performance and reversibility and steep switching gradient [21].

Polymer chain size and structure, as well as the type of solvent, affect the swelling/deswelling kinetic of thermosensitive systems. For instance, Wang et al. [26] showed poly(N-isopropylacrylamide) (PNIPAm) microgels in the presence of glycerol had lower thermosensitive response speed, since the presence of other molecules in the medium alters the hydrophilic and hydrophobic balance of the system. PNIPAm has been used as thermotropic component of SW [26,27] to respond to sunlight irradiation [19], change their optical properties by applying a high-frequency AC current [28], as well as a sweating component to passively cool buildings [29]. Nevertheless, PNIPAm is always combined with other materials to have its critical temperature adjusted to be suited for switchable devices [2], increasing the cost and hindering the development of SW.

Another thermosensitive polymer that has gained prominence is the poly(N-vinylcaprolactam) (PNVCL, $(C_8H_{13}NO)_n$). Although its broad application has been in the biomaterials field [30], PNVCL is a promising material for SW. The main difference between PNVCL and PNIPAm is regarding their phase transition in water. PNVCL exhibits a type I critical miscibility in water, which LCST decreases and shifts towards lower polymer concentration with increased molecular weight. On the other hand, PNIPAm represents a type 2, which LCST is independent of the molecular weight and is hardly affected by environmental conditions [31], being usually modified by the presence of comonomers. In this way, the LCST of PNVCL can be shifted to lower or higher temperatures just by changing chemical composition as the addition of salts [32], different solvents, copolymers [33], presence of surfactants [34] or even changing polymer structure or its molecular mass [30,35]. The possibility of having versatile LCST values allow the application of PNVCL for several environmental temperatures.

Here, we demonstrate an innovative application by using PNVCL as active material in SW devices, taking advantage of its capacity to modify the device transmittance according to the temperature, which can be achieved by induced heating of conductive substrates. Thereby, the color/optical transmittance of the smart windows can be changed anytime, without the need to reach a switching threshold in response to intense solar heating, as found in many passively switching systems based on thermotropic materials [19,36].

Concurrently, we were able to propose a singular approach to produce switchable devices composed by a facile assembly of the components (transparent conductive substrates and active material) and operation system supported by an applied voltage. In comparison to other switchable devices based on thermosensitive polymers [15,27,28,37], we designed a versatile and highly efficient device system dependent of a heating stimulus induced by small input power, requiring less energy consumption and just a thin layer of PNVCL suspension to undergo a reversible process of color and optical properties.

2. Materials and methods

2.1. Materials

N-vinylcaprolactam monomer (NVCL, 415464, Sigma-Aldrich ≥ 98%, USA) and dimethyl sulfoxide (p.a., ACS reagent, Synth, Brazil) were used as received. The 2,2′-azobis(2-methylpropionitrile) initiator (AIBN, DuPont, Brazil) was previously recrystallized in methanol. Switchable devices were constructed with transparent and conductive substrates made of fluorine-doped tin oxide (FTO) coated glass with a resistivity of 10 Ω/sq. and thickness of 1 mm (TCO10-10, Solaronix, Switzerland).

2.2. Synthesis and characterization of PNVCL

For the synthesis of PNVCL, NVCL monomer crystals were dispersed in dimethyl sulfoxide (15 wt%) and heated until 70 °C under N_2 atmosphere. Then, 2% w/w of AIBN initiator was dropwise added to the system and the reaction proceeded for 4 h. The PNVCL with Mn = 12.9 kDa was purified after being centrifuged and washed in hot deionized water for four times and dried at 60 °C in an lab oven with forced air circulation.

2.3. Smart windows building

Smart windows were built with two FTO substrates as a heating element and dynamical control of the temperature by bias applied. They were cut in square shapes with 2.5 cm of length and sealed with double-sided adhesive tape (VHB, 3 M Scotch® clear mounting tape 19 mm x 2 m, Brazil) and conductive liquid silver contacts (16062, PELCO® conductive silver paint, Ted Pella, USA), keeping the gap between the substrates of approximately 375 µm. Then, the device was filled with an aqueous solution with 1 and 5 wt% of PNVCL (Fig. 1) by using a syringe with a needle of 26 G, well-sealed with quick setting epoxy to avoid any leakage and drying out, and connected to a current voltage power supply unit (Hp E3611A power supply 0–020 VDC 1.5 A / 0–35 VDC 85 A 35 W).

2.4. Characterization

Liquid-state NMR experiments were performed on a Bruker Avance III spectrometer operating at a magnetic field of 9.4 T Oxford, with the related frequency of 400 MHz for the hydrogen-1 nucleus. Analyzes were performed with a tunable probe for a wide range of frequencies (40–160 MHz) and with 10 mm diameter tubes. PNVCL and its monomer were dispersed in 2.5 mL of water and chloroform, respectively, and D_2O and $CDCl_3$ were used as external standard. ^{13}C spectra were obtained qualitatively at room temperature in the fully coupled mode using NOE (Nuclear Overhauser Effect) transfer with an acquisition time of 0.55 s and relaxation time of 0.1 s.

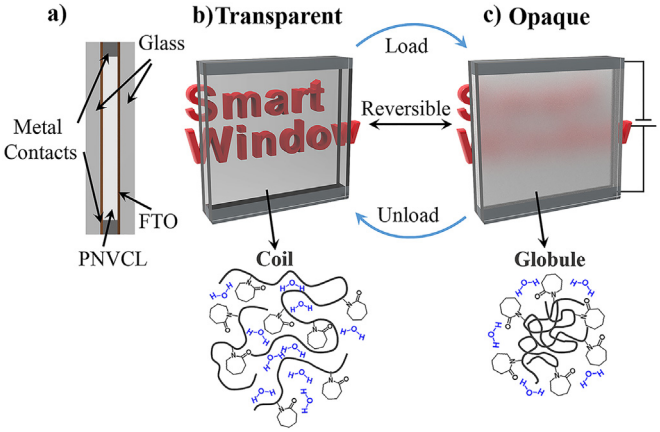

Fig. 1. Illustrative diagram of the smart window. (a) Assembly of two FTO substrates with a small gap filled up with PNVCL suspension. (b) Representative switch between transparent and opaque SW (c) during the coil-globule transition when applied a power supply.