'Smart' light-reflective windows based on temperature responsive twisted nematic liquid crystal polymers

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Abstract
'Smart' windows which reversibly increase their reflectivity upon heating are attracting considerable attention as devices for maintaining comfortable indoor environmental conditions. In this work, twisted nematic semi-interpenetrating liquid crystal networks which lose their order upon heating are sandwiched between reflective linear polarizers. This 'smart' window reversibly decreases its transmission from about 50–10% over a wavelength range between 400 and 1100 nm upon heating, resulting in the window becoming darker and reflecting more light. This 'smart' window is potentially interesting for energy saving window applications where variation between privacy and visible light transparency states is required.

KEYWORDS
'smart' windows, light reflective devices, liquid crystals, semi-interpenetrating networks, temperature responsive polymers

INTRODUCTION
Given the Western world's primarily indoor lifestyles, there is a rising desire to connect with the outside world via increased fenestration, as windows enhance building (and vehicle) appearances, and allow access of daylight and external views.1 Access to daylight is an important environmental factor affecting the health and well-being of people in home- and workspace,2,3 affecting both emotional and motivational states.4 As a result, the development of windows with additional functionalities, including privacy states or self-regulating solar heat rejection to prevent
overheating of room interiors, is an emerging research field.\textsuperscript{5–9} In particular, windows which autonomously change their transmission in response to changes in temperature are of special interest for maintaining comfortable indoor climates, while simultaneously reducing the energy loads required for artificial heating and cooling.\textsuperscript{10–16}

These switchable windows which can alter their transmissive states in response to temperature have been labeled as ‘smart’, and most are based on inorganic materials.\textsuperscript{12} Thermochromic windows rely on light absorption\textsuperscript{17} or scattering,\textsuperscript{6,12,18–22} forming ‘dark’, translucent, or reflective phases to manage the passage of light.\textsuperscript{60}

Organic-based thermochromic ‘smart’ windows have also been reported that switch between reflective and transparent states, scattering and transparent states, or from narrow- to broadband reflecting states. These ‘smart’ windows are generally based on polymer dispersed liquid crystals (PDLCs) or polymer stabilized liquid crystals (PSLCs) containing low molecular weight LCs able to undergo a re-arrangement upon temperature changes.\textsuperscript{23–41}

Our previous reflective LC-based windows utilized a shift in reflective bandwidth upon heating\textsuperscript{31} to control light transmission. In this work, we report a novel LC polymer-based ‘smart’ window which reversibly increases reflectivity upon heating. This reflective ‘smart’ window relies on a temperature-responsive noncross-linked liquid crystal elastomer (LCE) interpenetrating through a liquid crystalline network (LCN)\textsuperscript{42–44} sandwiched between two reflective linear polarizers. The semi-interpenetrating network (semi-IPN) window is effective over a broad wavelength range, including the visible light region (Figure 1(A)). Below the nematic-to-isotropic transition temperature (T_{N-I}) of the twisted nematic LC, the linear polarization (LP) of the light transmitted by the first reflective polarizer is rotated by the LC host and transmitted through the second polarizer, resulting in an in theory 50% overall reflection over the wavelength regime for which the linear polarizers are operative. Above the T_{N-I}, the LC loses order and is unable to rotate the LP light transmitted by the first polarizer, and so the

\begin{figure}
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\includegraphics[width=\textwidth]{figure1.png}
\caption{(A) Schematic drawing of the reflective ‘smart’ window. The double headed black arrows indicate the polarization direction of the reflective polarizers and the yellow arrows indicate the path of the traveling light. The LCs are ordered in a twisted nematic fashion below the T_{N-I} (blue bars) and less ordered above the T_{N-I} (red bars). (B) Chemical structures of the compounds used. LSc, liquid crystals [Color figure can be viewed at wileyonlinelibrary.com]}
\end{figure}
remaining light is also reflected by the second polarizer, resulting in higher total reflection over the operative wavelength regime. Thermal simulations show that the energy saving potential of deploying these responsive ‘smart’ windows as automotive windows could be significant.

2 | EXPERIMENTAL

2.1 | Materials

LCE-1 ((4-methoxyphenyl 4-[hexyloxy]benzoate)siloxane dimethylsiloxane copolymer) and LCE-2 ((4-methoxyphenyl 4-[butoxy]benzoate)siloxane polymer) were purchased from Synthon Chemical GmbH & Co. Achiral monoacrylate RM-1 ((4-methoxyphenyl 4-((6-[acryloyloxy]hexyl)oxy)benzoate), and achiral diacrylate RM-2 (1,4-phenylene bis (4-((6-[acryloyloxy]hexyl)oxy)benzoate)), were purchased from Merck. Chiral diacrylate RM-3 ((R,R)-1,4-di-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy)benzene) was obtained from Philips Research lab. The photoinitiator Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one) was purchased from Ciba.

2.2 | Methods

2.2.1 | Rubbed polyimide coated glass substrates

Glass slides (3 x 3 cm²) were cleaned by ultrasonication in ethanol for 30 min and subsequently exposed to a UV-ozone (UVP PR-100) treatment for 20 min. A polyimide (JSR Optmer AL1051) layer was spin coated on these glass substrates by rotating at 1000 rpm for 5 s, followed by 5000 rpm for 40 s using a Karl Suss CT 62 spin coater. After spin coating, the substrates were placed on a hotplate at 100°C for 15 min and subsequently placed in an oven at 180°C for 90 min. The cured polyimide glass substrates were rubbed over a velvet cloth before use.

2.2.2 | Fabrication of reflective ‘smart’ windows

Twisted nematic LC cells were fabricated by gluing two polyimide glass substrates in a perpendicular fashion using UV-curable glue (Norland Products Inc UVS 91) containing 6 μm polystyrene beads (Sekisui). The glue was placed on two opposite edges of one substrate and the substrates were pressed together using clamps and cured using a low intensity UV-lamp (4 Philips CLEO 15 W lamps) for 30 min. The LC mixture components were weighed in the desired ratios and subsequently dissolved in dichloromethane (50 wt%). About 40 μl of the solution was placed on a microscope slide on a hotplate (40°C) to evaporate the solvent. The LC mixture was filled in the twisted nematic LC cell overnight in the nematic LC phase by capillary action on a hotplate of about 55°C. After filling, the LC mixture was photo-polymerized in 10 min with an EXFO Omnicure S2000 mercury lamp UV light (16 mW/cm²). Subsequently, two reflective linear polarizers (3 M DBEF films, Figure S1) with adhesive layer on one side were placed following the alignment direction of the twisted nematic LC cell.

2.2.3 | Differential scanning calorimetry

Transition temperatures of the LC mixtures were measured using a TA Instrument DSC Q2000. Measurements consisted of 3 cycles at a rate of 5°C/min.

2.2.4 | UV/Vis/NIR spectrophotometry

Temperature-responsive transmission spectra were measured on a Shimadzu UV-3102 PC UV/Vis/NIR spectrophotometer equipped with an MPC-3100 sample compartment and a Linkam TMS93/LMP93 temperature control stage. Two glass slides were used as baseline measurement. The transmission spectra at room temperature were also measured on a Perkin Elmer Lambda 750 UV/Vis/NIR-spectrophotometer. This spectrum was used to correct for the detector change artifact observed in the temperature-responsive spectra of this ‘smart’ window. Angular dependent measurements were also performed on the Perkin Elmer spectrophotometer equipped with an ARTA accessory that utilizes a 60 mm integrating sphere mounted on a goniometer with PMT and InGaAs detectors.

3 | RESULTS AND DISCUSSION

3.1 | Preparation of the temperature responsive light-reflective windows

The temperature responsive twisted nematic liquid crystal polymer systems contain a chiral liquid crystalline network (LCN) interpenetrating through a noncross-linked liquid crystal elastomers (LCE) and rely on temperature-responsive behavior of the LCE as reported earlier. For preparing the first ‘smart’ window, we filled a 6 μm twisted nematic LC cell with a mixture containing LCE-1 (82.6 wt%), monoacrylate RM-1 (13.2 wt%), diacrylate RM-2 (2.8 wt%) and chiral diacrylate RM-3.
(0.4 wt%). The second smart window sample contained LCE-2 (83.6 wt%), monoacrylate RM-1 (13.4 wt%), diacrylate RM-2 (1.6 wt%), and chiral diacrylate RM-3 (0.4 wt%). The structures of all the molecules are found in Figure 1(B). The chiral diacrylate was used to induce the rotation of consecutive LC planes. A photoinitiator (Irgacure-651, 1 wt%) was added to allow photopolymerization of the acrylates to form a network. After photopolymerization with UV-light, we prepared the ‘smart’ windows by sandwiching the twisted nematic LC cell between two reflective linear polarizers following the LC director (Figure 1(A)).

3.2 Characterization of the temperature responsive light-reflective windows

We first characterized the temperature responsive optical device based on the semi-IPN containing LCE-1. Below the T_{N-1} of the twisted nematic LC, LP light transmitted by the first polarizer is rotated by the twisted nematic LC and is transmitted through the second polarizer (the T_{N-1} of the unpolymerized LC mixture is 38°C, Figure S2). As a result, the ‘smart’ window transmits between 40 and 50% of incoming unpolarized light over the wavelength range for which the polarizers are designed (400–1100 nm, Figure 2(A) and (B)). Note that the irregularities in the transmission spectra can be attributed to imperfections of the reflective linear polarizers and measuring apparatus (Figure S1).

When heated above T_{N-1}, the LCE loses order and the LC is no longer able to efficiently rotate the LP light transmitted by the first polarizer, and thus encounters the second polarizer with the polarization direction rotated with respect to the polarizer transmission axis, and thus is partially reflected. Because of this, the transmission decreases to approximately 10% over the entire wavelength range upon heating to 69°C (LCE-1, T_{N-1} = 58°C), thereby reducing transmission through the ‘smart’ window (Figure S3). The ‘smart’ window was demonstrated to be reversible over at least 7 cycles of heating and cooling (Figure 2(C)). The transmission of the window is dependent on the incidence angle of the incident light.
light with somewhat decreased transmission at larger oblique angles (Figure S4). This is likely the result of generation of elliptical polarization of the light by the LC.

The transition temperature of the ‘smart’ window can be programmed by using an LCE with a different TN-I, allowing the window response to be tailored to the desires of the occupants and region of the world where the window is deployed. As an example, we produced an additional ‘smart’ window using an elastomer with a lower transition temperature (LCE-2, TN-I = 40°C). This resulted in a reduction of the TN-I of the unpolymerized mixture to 26°C (Figure S5). The device started to decrease its transmission above 30°C, which is 5°C lower compared to the ‘smart’ window prepared with LCE-1 (Compare Figure 3 with Figure 2).

3.3 | Computational study of overheating reduction in parked vehicles

The type of ‘smart’ windows we report here can potentially be deployed in a variety of application domains. In particular, the automotive industry appears to be a promising area because the interiors of automobiles may reach very high temperatures in sunny conditions unless steps are taken to reject the incident light.9 These ‘smart’ windows could be integrated in automobile rear-, side-, and roof windows to manage the passage of visible and/or IR light for enhanced thermal comfort for the passengers while maintaining passenger safety. Calculations of the visible and solar light transmittance show a clear contrast at various transition temperatures (Figure S6). Simulations were carried out using the software EnergyPlus, with a thermal model of a Tesla model S that was previously validated.9 Simulation results with the ‘smart’ window installed on the rear back-, back- and roof windows show that cabin temperatures of the vehicle parked in Amsterdam in June have an average maximum cabin temperature reduction of 3.3 and 6.7°C compared to a standard automotive glass type for external temperatures of 35 and 69°C, respectively (Figure S7). These results indicate a significant potential of these light-reflective ‘smart’ windows to reduce automotive air-conditioning consumption and increasing the thermal comfort of passengers.

4 | CONCLUSION AND OUTLOOK

We demonstrate the working principle of a novel reflective ‘smart’ window. The device relies on the reversible decrease of order of a noncross-linked LCE interpenetrated through an LCN upon heating. We sandwiched a twisted nematic semi-IPN network between two reflective linear polarizers, resulting in a reflective ‘smart’ window which reduces its transmission from about 50–10% over a wavelength range between 400 and 1100 nm. We show that the transition temperature of the ‘smart’ window can be tuned so that the device can comply to the desires of occupants and different regions of the world.

Thermal simulations of a parked vehicle show that the ‘smart’ windows can reduce the cabin temperature by 3–7°C when replacing normal automotive glass windows with the ‘smart’ windows on the rear back-, back- and roof windows of a car, revealing the energy saving potential of this method.

To comply with safety regulations and user demands, future research should focus on controlling the level of transmission change. In addition, the ‘smart’ windows
show a reflective appearance due to the reflective polarizers used. Absorptive polarizers or a combination of an absorptive and reflective polarizer could be used to reduce this reflective appearance if desired. Furthermore, the scalability of the fabrication method of the ‘smart’ windows and their durability when exposed to outdoor weather conditions should be investigated to elucidate industrial feasibility.

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