Copolymer solution-based "smart window"

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The authors report the design of a prototype smart window based on the phenomenon of the thermally induced aggregation of triblock copolymer poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (EPE). Fluorescein isothiocyanate was used to label EPE and study aggregation phenomenon at different temperatures. The cloud point could be tuned by mixing EPE with sodium dodecyl sulfate (SDS) and varying the concentration of the later. The light transmittance at different temperatures was studied as a function of SDS concentration. © *2009 American Institute of Physics*. [doi:10.1063/1.3276289]

The smart window is a system that can sense and respond to external stimuli such as light, heat, or electricity. It controls light passage through its glass, promising the advantages of reversible control of indoor light and temperature in applications to next-generation household or industrial windows for the multiple purpose. Various systems over the years have been tested. The materials used in these systems can be generally classified into following three categories: electrochromic,[1,2] thermochromic,[3] and photochromic materials.[4,5] For example, the electrochromic window is composed usually of liquid crystal sandwiched between two panes of glass or plastic that is coated with indium tin oxide (ITO), a transparent conductive material. When an electrical current passes through this window, the particles change their orientation, which either allows light to, or prevents it from, passing through. The thermochromic smart window, typically a vanadium dioxide (VO_2)-type window, structurally transits from a semiconductor to a metal at a critical temperature Tc. This transition accompanies an abrupt change in optical properties, which can block light. Generally, these allochromatic materials are either organic molecules with specific grafting groups or metal transition oxides. Although smart windows composed of these materials have the advantages of high color contrast, flexible switching speed, and low response time, among others, the high cost of material synthesis limits their practical applications, for example, to family sunlight screens or temperature response. In the present research, we studied, as an alternative to chemical composition change or phase change, the influence of molecular self-assembly (aggregation) on light transmittance. Thermally induced self-assembly of poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (PEO-PPO-EPE) triblock molecules (EPE) were introduced. EPE is a type of easily available triblock copolymer that is widely used as a nonionic surfactant, due to its amphiphilic behavior in aqueous solution. There are a variety of types of EPE, which are differentiated by their overall molecular weight and the ratio of the hydrophobic PPO block length to the hydrophilic PEO block length. These molecules, owing to the dehydration of PPO, can self-assemble into micelles in aqueous solution above the critical micellization temperature.[6] The hydrophobic PPO blocks form the micelle core, which is surrounded by an outer water-swelled coronal shell composed of hydrophilic PEO chains. A possible structure is shown in Figs. 1(a) and 1(b).[7] Alternatively, with increasing temperature, the micelle can further form clusters through entangling with the hydrophilic coronal PEO chains. It has also been reported that if the molecular weight of the PEO chains is far below the critical molecular entangle weight of 1600, the micelle clusters are still present simply by close packing of micelles without entanglement [Fig. 1(c)].[8] In the cluster state, the dissolved solids are no longer completely soluble, precipitating as a second phase and manifesting a cloudy appearance. The cloudy appearance is induced by increasing temperature, and the temperature at which the cloudiness appears is termed the cloud point. Such a phenomenon is reversible if the temperature regains. The cloud point is slightly adjustable by adding an electrolyte, for example, sodium chloride.[9] In the present study, in order to adjust the cloud point, we used an alternative amphiphilic molecule, sodium dodecyl sulfate (SDS) as a cooperative surfactant to regulate the phase separation of the EPE copolymer.

We used 1 v/v % aqueous solution of EPE (total average molecular weight: 2000; molecular PEO weight: <1600, Sigma, used all through this work) with 0.5 v/v % SDS added as medium to control the passage of light through the smart window. Properties of this solution were first examined with different temperature. We prepared EPE solution without SDS. Under 23 °C, the solution maintained perfect
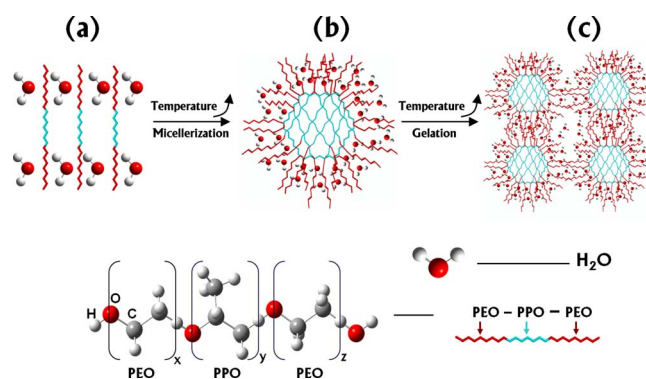

FIG. 1. (Color online) (a) EPE molecules dispersed in water when no heating applied. (b) Increasing the temperature leads to the formation of micelles. (c) Further increasing the temperature leads to the packing of micelles to form clusters.

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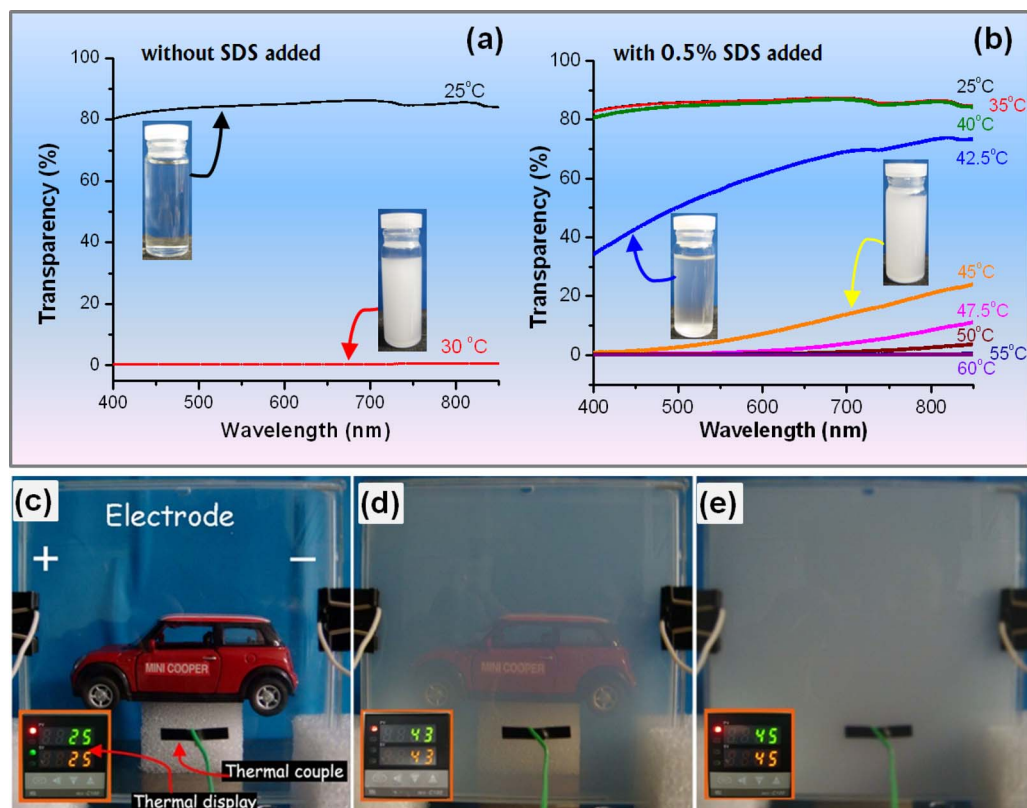
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FIG. 2. (Color online) Transparency measured at wavelength from 400 to 800 nm of (a) 1 v/v % aqueous solution of EPE without SDS added, (b) 1 v/v % aqueous solution of EPE with 0.5 v/v % SDS added. Smart window fabricated by sandwiching EPE liquid between two pieces of ITO glass at (c) room temperature, (d) 43 °C by applying a voltage, and (e) 45 °C.

transparency [Fig. 2(a)]. However, at 30 °C, the solution was completely light-tight, as shown in the Fig. 2(a) insets. We then added 0.5 v/v % of SDS, which is supposed to advance the EPE cloud point. From 23 to 40 °C, the transparency did not change a lot, the solution retaining an appearance likeable to pure water [Fig. 2(b)]. At 42.5 °C, some turbidity could be observed, and after the temperature was raised to 45 °C, the solution became completely light-tight [Fig. 2(b)]. In constructing the smart window system, we sandwiched EPE between two ITO-sputtered glasses with a gap of 1 mm and applied a voltage to impart Joule heating. A thermal couple was used for temperature feedback. The temperature could be controlled by adjusting the intensity of the electrical current. In order to demonstrate the "smart" function of the window, we placed a model car behind the glass window. At room temperature, the window was transparent and the car, accordingly, was clearly visible [Fig. 2(c)]. But when the glass was heated to the cloud point at 43 °C, the resultant turbidity gave the window a cloudy appearance, and the profile of the model car became obscure [Fig. 2(d)]. After further heating the glass to 45 °C, the window screened most of the light, the window becoming completely opaque, no background being visible [Fig. 2(e)]. This process is reversible. Switching off the electrical current and cooling the system to room temperature, the glass window will recover its original state with good transparent character within several minutes, depending on how fast the temperature can be lowered.

The principle of the smart window is straightforward. At low temperature, the copolymers are dissolved into individual molecules [Fig. 1(a)]. When the solution is heated to

the critical micellization temperature, the EPE molecules begin to form micelles [Fig. 1(b)] and the size of the micelles becomes larger and finally saturated as the temperature is further increased.[10] This trend is partially due to the enhanced hydrophobicity of both the PPO and the PEO chains when they are dehydrated with increasing temperature. Once
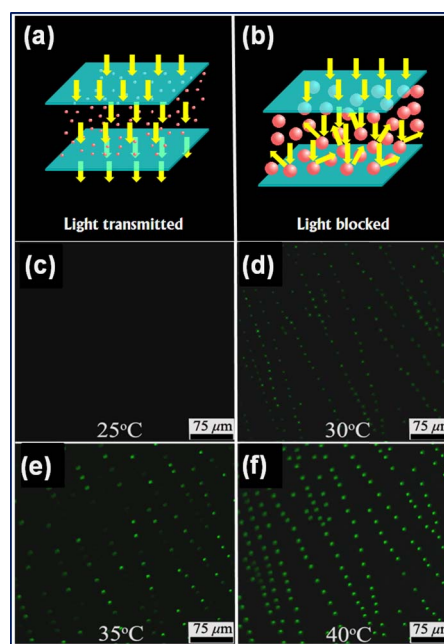

FIG. 3. (Color online) (a) and (b) are schematic pictures to demonstrate the relationship between particle size and light passage. [(c)–(f)] Fluorescent spots detected under different temperature.
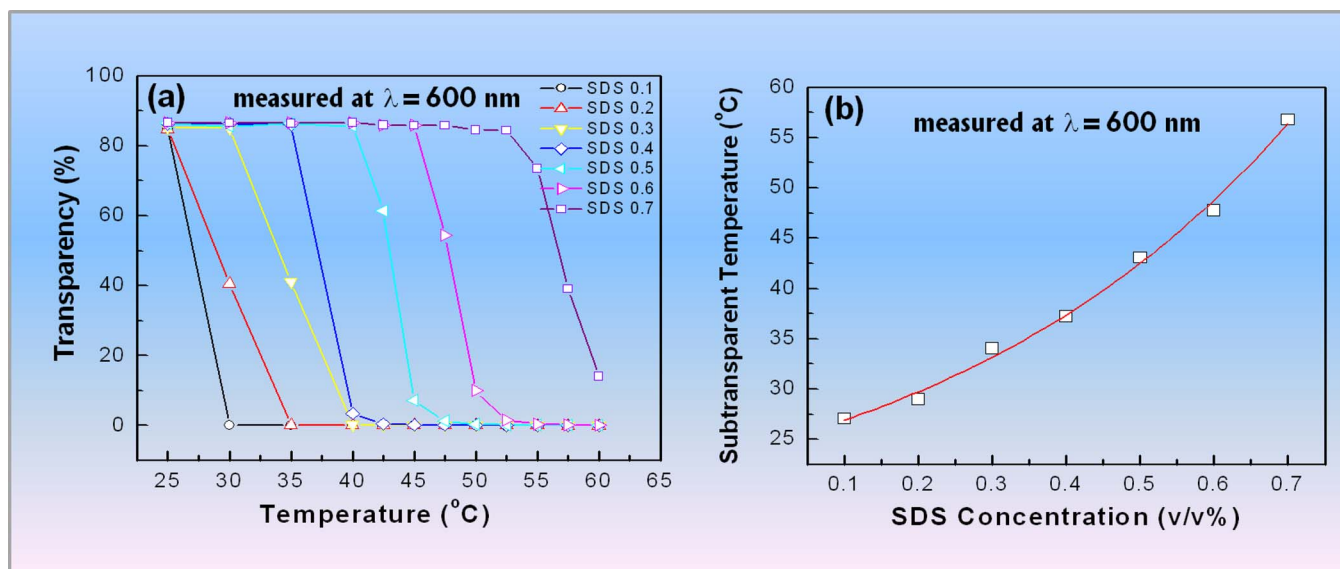
FIG. 4. (Color online) Influence of SDS concentration on transmittance of EPE aqueous solution measured at (a) 600 nm. (b) Influence of SDS concentration on subtransparent temperature.

the cloud point is approached, the micelles aggregate into large clusters [Fig. 1(c)], whose morphology is believed to be the cause of the turbid appearance. The whole process is accompanied by a transmittance change that enables complete opaqueness of the solution at the cloud point, thereby blocking radiation such as sunlight [Figs. 3(a) and 3(b)]. To reveal the micelle cluster formation, a trace amount of fluorescent isothiocyanate (FITC) (green fluorescence) was dissolved into 1 v/v % aqueous solution of EPE, and the fluorescence was imaged under an inverted fluorescence microscope (Axiovert 200 M, Zeiss) equipped with a cooled charge-coupled device camera (Diagnostic Instruments). The amphiphilic nature of FITC is the source of its affinity for EPE molecules and also, thus, the rationale for its use in EPE-molecule labeling.[11] Liquid was laid deposited on an ITO glass that was connected to electrodes for heating. Below the cloud point at 24 °C, there were no fluorescent spots detected [Fig. 3(c)]. But after heating the liquid to a temperature above the cloud point, micron-sized fluorescent clusters could be observed [Fig. 3(d)]. After continuing to increase the temperature, we could detect an intensification of the fluorescence, induced by the further aggregation of micelles [Figs. 3(e) and 3(f)], leading eventually to the turbidity of the solution. These micron-sized micelle clusters have also been found in other EPE solutions of lower-than-1600 molecular PEO weight.[12]

We chose SDS as a cloud point modifier because it can affect, in two ways, both the formation of EPE micelles and the agglomeration. First, the binding of ether SDS monomers or micelles with PPO chains prevents the dehydration of the PPO chains, thus destabilizes the EPE micelles.[13] Second, an electrostatic repulsive interaction is introduced between the EPE-SDS mixed micelles in addition to the originally attractive force. The attractive force arises partially from the enhanced hydrophobicity of PEO chains and is the main driving force of close packing of micelles into clusters.[10,14] To estimate the effect of SDS in modifying the cloud point, we chose EPE having an average molecular PEO weight lower than 1600, in order to lessen the entanglement of PEO chains

and facilitate the interposition of SDS.[8] We mixed 0.1–0.7 v/v % of SDS into 1 v/v % of EPE solution. The sunscreen efficiency of the liquid was determined by measuring the light transmittance as a function of temperature at ranges of visible light [Fig. 4(a)]. To show the effect of SDS in improving cloud point, the subtransparent transparency as a function of SDS concentration was drawn as shown in Fig. 4(b). With the increasing SDS concentration, the temperature at which the liquid attained its subtransparent state shifted remarkably to a higher region. Cloud point modification was shown, thus, to be a potential means of actively controlling the passage of light through the solution. The shift of the cloud point to a higher temperature prevented the turbidity of the solution at room temperature, without addition of SDS.

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