RAPID COMMUNICATION

Grafted radical polymer brush for surface-driven switching of chiral nematic liquid crystals

Redox-active polymers have received considerable attention as candidate components in the next generation of soft and environmentally friendly electrochemical devices, including secondary batteries, electrochromic cells and memory.[1–3] In particular, polymers having a well-defined architecture have been shown to exhibit unique chemical and physical properties. For instance, surface-grafted brush polymers provide fast long-distance charge transport, enhanced mechanical strength and longer redox cycles based on their precisely controlled architectures.[4–6] Bottlebrush polymers, which are characterized by intrinsic stiffness and high solubility in electrolytes, have been found to be useful as active materials for redox flow cells.[7] Further, the brushes have been applied to new devices and systems, such as highly sensitive biosensors, electrochemical switching of surface tension, and formation/deformation of micelles.[8–10]

In this study, we propose a new technique to switch the orientation of nematic and chiral nematic liquid crystal electrolytes, which proceeds simultaneously with the redox reactions of the surface-grafted polymer brushes (Figure 1a). A chiral nematic liquid crystal phase characterized by a helical structure of self-assembled molecules displays interesting optical properties, including light reflection with wavelength selectivity and circular polarization.[11–14] The helical structures are applied to optical filters, displays, lasers and even metamaterials.[11–14]

Control of alignment is more challenging for chiral nematic phases than for normal nematic phases. Orientation of the nematic phases is easily switched by application of an external magnetic or electric field, utilizing the anisotropic electromagnetic properties of the liquid crystal molecules.[15] However, the helical structures of the chiral nematic phases are normally broken when an electromagnetic field is applied (that is, the cholesteric-nematic transition, Figure 1b).[15]

The present study focuses on 'command surface'[16] switching of nematic liquid crystals to maintain the original helical structure. In the neutral state of the redox sites, planar alignment is obtained due to the van der Waals force between the polymer electrode and the liquid crystal. However, after oxidation/reduction of the redox-active moieties, homeotropic alignment can be observed because of the electrostatic interaction between the dipole moment of the liquid crystal and the electric field in the double layer, which is formed in the vicinity of the electrically charged polymer electrode.[17,18]

Although previously reported switchable liquid crystals have been limited to only nematic phases, this study revealed that even the alignment of chiral nematic phases could be controlled using redox-active polymer brushes. In contrast to the conventional method, the helical structures of the chiral phase were maintained even when an external voltage was applied, because the electric field existed only in the vicinity of the electrodes due to the presence of electrolyte ions and the electrical double layers. Furthermore, the required voltage (2 V) to induce the electrochemical reaction and switching was substantially lower than that of the conventional method (10^{1-2} V), which is favorable for low-power devices.
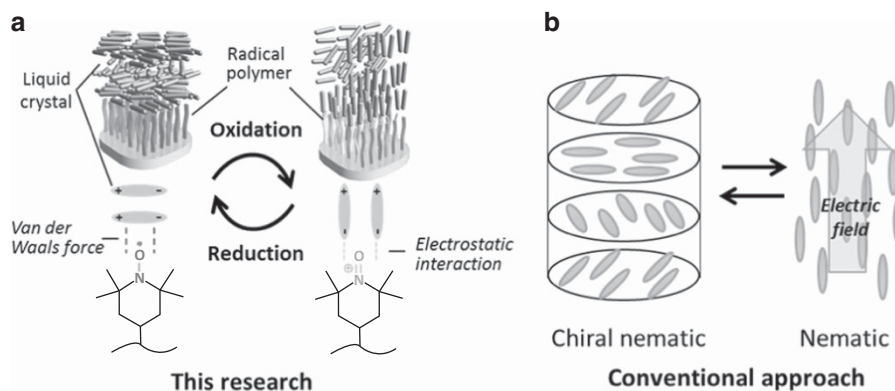
Figure 1 (**a**) Surface-driven switching of chiral nematic liquid crystals by radical polymers. (**b**) Cholesteric-nematic transition induced by external electric field. A full color version of this figure is available at the *Polymer Journal* online.

A redox-active polymer, poly[2,3-bis (2′,2′,6′,6′-tetramethylpiperidin-1′-oxyl-4′-oxycarbonyl)-5-norbornene] (PTNB), was grafted onto an indium tin oxide (ITO) glass substrate by surface-induced ring-opening metathesis polymerization (ITO-g-PTNB, Scheme 1). Previously, we reported a series of aliphatic polymers whose side chains were substituted with redox-active, robust radical groups such as TEMPO.[3,4,7,19] The radical polymers yielded remarkably fast and reversible redox reactions due to their non-conjugated design and electrochemically reactive radical centers. Use of the third-generation Grubbs catalyst enabled the precise synthesis of PTNB by living polymerization.[7,19] The surface grafted polymer showed the same spectroscopic characteristics as the conventional polymer prepared by homogenous polymerization in solution,[19] strongly suggesting the successful completion of the reaction (Supplementary Information). The decreased roughness of the substrate after the polymerization suggested dense grafting

of the radical polymer chains (Supplementary Figure S1).

The obtained polymer brush provided highly reversible redox waves at 0.35 V (vs ferrocene/ferrocenium) in an acetonitrile solution of tetrabutylammonium perchlorate with a three-electrode system (Figure 2a). The peak separation was < 10 mV even at a relatively high scan rate of 10 mV s^{−1} for a polymer layer.[19] The remarkably fast charge mediation throughout the brush polymer[4,7] provided a Nernstian adsorbate-like bulk layer[19] as an electrode. In contrast, in case of the spin-coated polymer layer, the monolayer response was observed at only sufficiently slow scan rates (< 1 mV s^{−1}),[19] probably because of the different molecular architecture and charge transport properties.[4] We note that precise control of the electric charge throughout the polymer layer is crucially important for the switching of liquid crystals because the alignment is determined by the surface charge of the polymer electrode. The obtained electrode capacity of

0.11 mC cm^{−2} for the polymer brush layer corresponded to the introduction of ~7 redox sites per 1 nm[2] of electrode area, suggesting the successful surface grafting of the polymer.

Next, we fabricated a two-electrode cell consisting of the ITO-g-PTNB electrode as the working electrode, a double-layer capacitor electrode as the counter electrode,[17] and a chiral nematic liquid crystal as the electrolyte. The electrolyte solution was a mixture of a typical nematic liquid crystal, 4-cyano-4′-pentylbiphenyl (5CB) with positive dielectric anisotropy, an ionic liquid, 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB)[17] and a chiral inducer (CI)[20] (Figure 3). Polarization microscopy suggested that planar alignment of the liquid crystals was achieved in the neutral states of the polymer because of the van der Waals force (0 or −2 V, Figure 2b). In contrast, when 2 V was applied to the cell, a fingerprint texture of the chiral nematic phase was observed, meaning that the orientation was switched by 90° (that is, homeotropic alignment of the liquid crystal molecules against the substrate). The oxidized and cationic TEMPO moieties in the polymer induced the formation of an electrical double layer in the vicinity of the electrode to vertically align the liquid crystals. Likewise, the redox-induced switching was achieved with the nematic liquid crystal phase, supporting the versatility of the technique (Figure 2c). The time required for switching was within several seconds. The remarkably fast charge transport throughout the polymer enabled such rapid switching of the surface charge and liquid crystal alignment. The homeotropic alignment was maintained even with an open circuit (that is, bistable) because
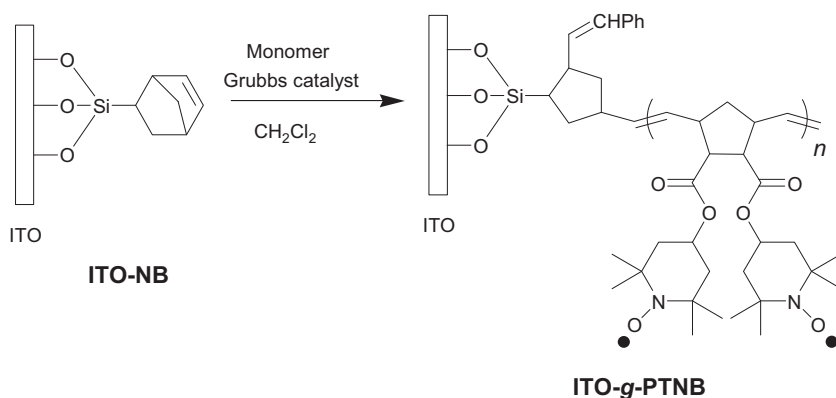
Scheme 1 Preparation of surface-grafted PTNB.
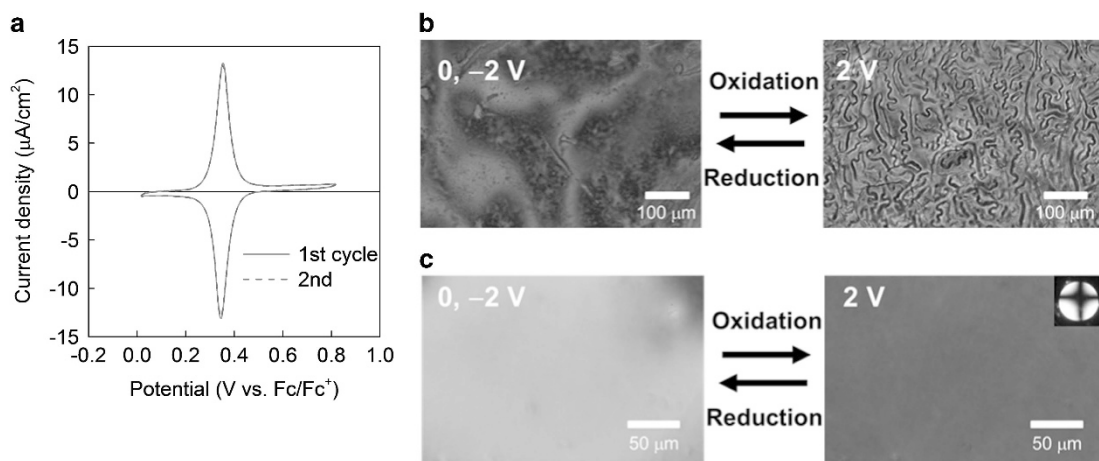
Figure 2 (a) Cyclic voltammogram of ITO-g-PTNB measured in 0.1 M n-C$_4$H$_9$NClO$_4$ in acetonitrile; scan rate, 10 mV s^{−1}. (b) Polarized light microscopy (POM) of a chiral nematic liquid crystal (EMIM TCB/5CB/CI = 0.7/100/0.25 (mol/mol/mol) cell. (c) POM of a liquid crystal cell without chiral inducer. Inset: Conoscope image. The cross-shape indicates the homeotropic alignment. A full color version of this figure is available at the *Polymer Journal* online.
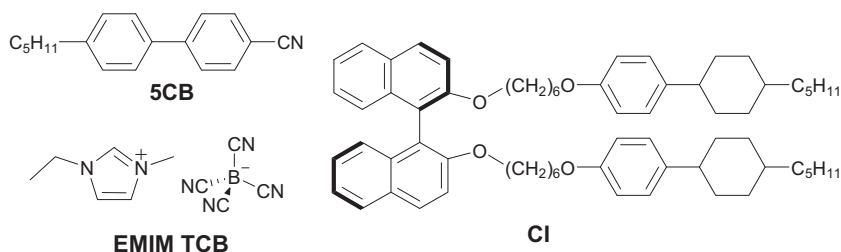
Figure 3 Structures for chiral nematic liquid crystal electrolytes.[20]
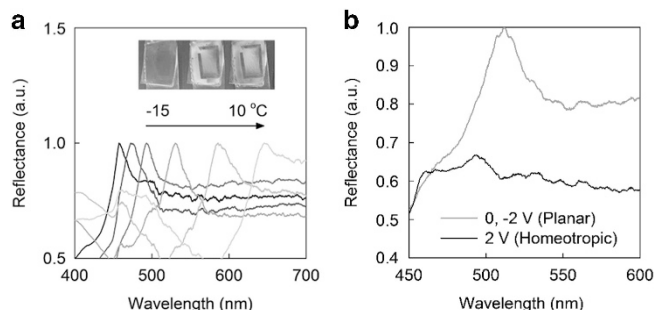
Figure 4 (**a**) Reflectance of a chiral nematic liquid crystal cell measured at − 15, − 10, − 5, 0, 5, and 10 °C. Inset: photograph of the cell at − 15, 0 and10 °C. (**b**) Reflectance of the cell with planar and homeotropic alignment of the liquid crystals at 0 °C. The electrolyte was EMIM TCB/5CB/CI = 0.7/100/8 (mol/mol/mol). A full color version of this figure is available at the *Polymer Journal* online.

of the stable doped state of the polymer and the retention of the surface charge.[3]

Finally, the display characteristics of the chiral nematic cell were examined. By increasing the amount of the chiral inducer from 0.25 to 8 mol %, the spiral pitch decreased to the order of 10^2 nm and selective reflectivity of visible light was achieved. The color of the liquid crystals changed from blue to red continuously depending on the cell temperature and the chiral pitch (Figure 4a).[11] The redox reaction of the polymer switched the direction of selective reflection. In the neutral state of PTNB (0, − 2 V), the liquid crystal was oriented in a planar direction. Therefore, light perpendicularly incident on the cell was reflected with wavelength selectivity (Figure 4b). However, in the cation state, the light was no longer reflected because the alignment of the liquid crystals was rotated by 90º. To our knowledge, this is the first such report of an electrochemical, surface-driven switching of the chiral nematic phase.

In summary, we demonstrated that a redox-active polymer brush functioned as an electrochemical command surface for reversible switch alignment of chiral nematic liquid crystals with light reflection. Our next goals will be to better understand the detailed processes of the technique and to fabricate low-power chiral liquid crystal displays with high pixel density.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)