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Chirality-Driven Wettability Switching and Mass Transfer**

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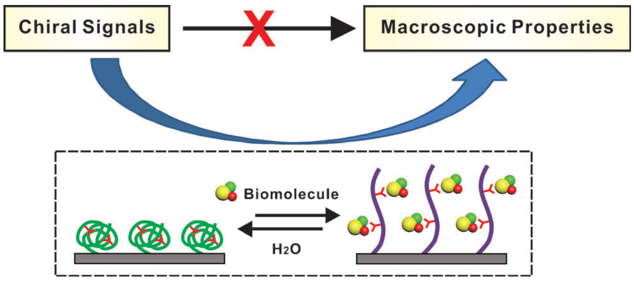
Since Pasteur proposed the concept of chirality in 1848,[1] chirality and relevant studies have always been a hot topic in chemistry, physics, and biology. In materials science, chiral surfaces have also emerged as a rapidly developing field,[2] and has many attractive features for applications in sensors,[3a] medicines,[3b] biotechnology,[3c–f] catalysis,[3g] etc. In general, these features originate from the stereoselective chemical or physical interactions with other chiral molecules or matrices. However, the signals of chiral interaction are usually very weak, thus making it difficult to directly correlate to macroscopic properties of materials, except for optical properties, and restricts their practical applications.[4]

Fortunately, the appearance of smart polymers, especially those responsive to biomolecules in solution, developed in recent years, provides an ideal platform to bridge this gap (Scheme 1).[5] By taking advantage of a "recognition-mediating-function" (RMF) design concept for smart copolymers, biomolecule recognition events can be translated into the conformational transition of polymer chains by synergetic hydrogen-bonding (H-bonding) interactions, which induce reversible switching of macroscopic properties of materials.[6]



Scheme 1. Conformational changes of smart copolymers provide an ideal platform to bridge the gap between chiral signals and macroscopic functions of materials.

Inspired by such a RMF design concept, a novel three-component smart copolymer brush film capable of responding to chiral signals has also been developed.[7] It is composed of dipeptide-based chiral recognition units, phenylthiourea-based mediating units, and a flexible poly(*N*-isopropylacrylamide) backbone as the functional switching units. The copolymer film was originally hydrophobic with a contact angle (CA) of about 105° because of the shrunken hydrophobic state of the copolymer brushes. After being immersed in an aqueous solution of L-lyxose for several minutes, the CA value decreased to about 66°, and in contrast, a D-lyxose solution with the same concentration induced a larger decrease of the CA to about 53°. By taking advantage of the magnification effect of surface micro- or nanocomposite structures on wettability,[8] the difference in the CA values was further amplified on a textured substrate, thus resulting in chirality-triggered wettability switching between superhydrophobicity ($CA \approx 155°$) and high hydrophilicity ($CA \approx 30°$). This report is the first on chirality-driven wettability switching on a solid surface. Mechanistic studies indicated that the binding between dipeptide units and L- or D-lyxose could break the intramolecular H-bonds to different extents, thus giving different relaxed conformations (Figure 1a) of the copolymer chains. Since all the interactions were accomplished by H-bonds, the wettability switching exhibited excellent reversibility, which has potential advantages for applications. In contrast, the RMF design principle also makes it easy to change the copolymer structures and thus realize responses to other chiral molecules.

Recently, by utilizing a similar principle, Shundo, Tanaka, and co-workers from Kyushu University (Japan) extended this research to chiral liquids.[9] They constructed a chiral polymer film with four distinct units, main chain of methacrylate, alkyl linkers, biphenyl moieties, and alkyl chains having a chiral center, and reported that the chiral liquid [(*R*)- or (*S*)-1,2-propanediol (PD)] induced wettability switching. According to their report, (*R*)-PD could penetrate into the polymer film and induce an obvious conformational change, thus resulting in a CA decrease with an increase of time, and finally reach a constant value of about 41° after 20 seconds. In contrast, (*S*)-PD did not induce any change in wettability (Figure 1b). The reliable evidence of conformational change was obtained in sum frequency generation vibrational spectroscopy, in which the authors clearly observed the H-bonding interactions between the carbonyl groups of polymer chain

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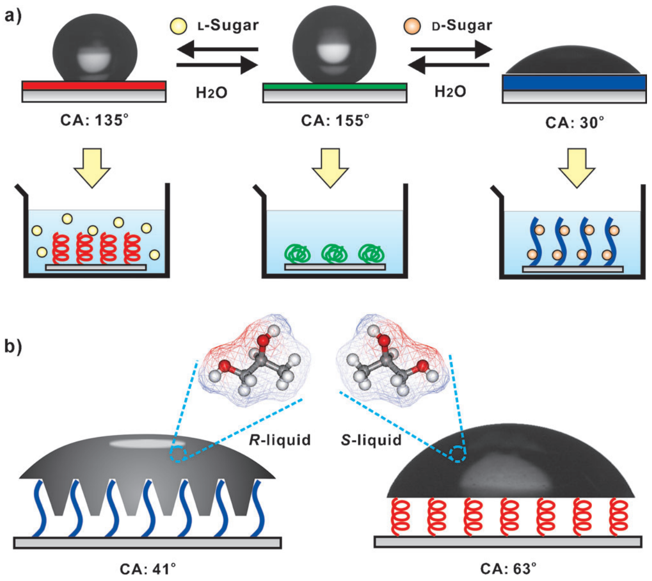

Figure 1. Wettability switching triggered by chiral sugars (a) (from Ref. [7]) and chiral liquids (b) (from Ref. [9]) on the polymer surfaces. Schematic diagrams for corresponding conformations of the polymer chains. Reproduced with permission from American Chemical Society Publishing.

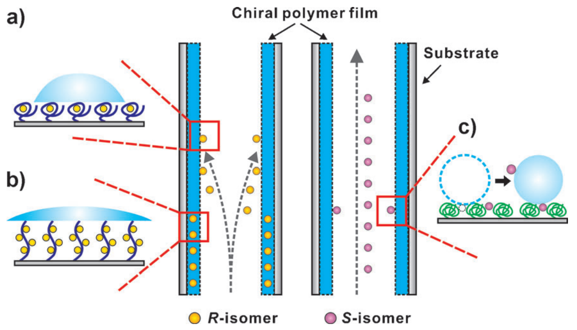

Figure 2. Dynamic adsorption processes of *R* or *S* isomers on the chiral polymer films. *R* isomers induce the relaxations of polymer chains and the increase of local wettability of surfaces (a), and further promote the adsorption of *R* isomers on the surfaces (b). The *S* isomers do not induce apparent changes in film properties and only exhibit weak adsorptions on the surfaces (c).

and the hydroxy groups in (*R*)-PD. These interactions are considered to be the main driving force for the reorganization of polymer chains. As a result, the polymer film became much rougher upon contact with (*R*)-PD, but no substantial change was observed when using (*S*)-PD. Considering the wide applications of chiral liquids (particularly ionic liquids) in chemistry, for example, solvents to perform special reactions, chiral catalysis, separation and purification, different wettability responses to chiral liquids may trigger some new applications.

Wettability is a fundamental property of materials surfaces, and directly determines the mass-transfer processes at solid/liquid interfaces, for example, adsorption dynamics, binding and release, etc.[10] The chirality-driven wettability switching described in the above-mentioned reports thus provides a novel strategy to control these processes by the chirality of molecules.[11] On the one hand, for applications such as chiral separation, chiral sensing, chiral catalysis, etc., these chiral molecules may also be the target molecules, reactants, products, or solvents themselves. On the other hand, mass-transfer processes at the interface directly determine the performance and even success or failure of these applications. Therefore, this property may bring many interesting and useful features for these applications.

For example, when it is used in chiral separation of enantiomers, a specific isomer (e.g. *R* isomer) may penetrate into the copolymer film, thus inducing the rearrangement of polymer chains and an increase of local wettability of the surface, whereas its antipode (*S* isomer) does not induce an apparent change in film properties. The difference in wettability further promotes or suppresses the adsorption of enantiomers on local surfaces (Figure 2), and can substantially improve the separation efficiency. Compared with conventional affinity chromatography, which is based on the affinity difference for enantiomers with chiral stationary phase, the difference in wettability and polymer chains is more remarkable and stronger, and may not only lead to the innovation of separation techniques,[12] but may also be especially useful for the separation of chiral compounds which are difficult by conventional methods.

Similarly, for the design of chiral sensors,[13] through the RMF design principle, weak chiral signals can be captured, translated, and amplified to various macroscopic properties of materials, including wettability, volume, morphology, rigidity, and even conductivity, when it is combined with a conductive polymer. All these properties can be read and processed more conveniently compared with optical or spectral techniques, and will reduce the reliance on equipment and complicated operations. In this aspect, the research of chiral helical polymers could provide valuable insights for molecule design and device development.[14]

Additionally, for chiral catalysis, the enantioselective wetting may also bring some beneficial factors.[3g,15] On the one hand, the smart polymer may combine more strongly with one chiral reactant but weakly with its enantiomer. This selectivity will substantially reduce the requirement of enantiomeric purity for reactants in the catalytic reaction. On the other hand, the combination with chiral reactants may induce the conformational transition of polymer chains and a favorable wettability change to further promote the enrichment of chiral reactants near the catalytic center, thus largely improving the catalytic efficiency.[16] Besides, different wettability responses upon using chiral liquids, which have been extensively used as solvents for chiral catalysis, it also makes it possible to control the reaction process dynamically and intelligently.

In summary, chirality-triggered wettability switching has been realized on smart-polymer surfaces based on the conformational changes of the polymer chains, and shows potential for both the fields of smart materials and chiral chemistry. However, the research is still in the early stages and there are still many opportunities and challenges for this interdisciplinary subject.

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