1 Introduction

Paper is a porous sheet material that is made of natural cellulosic fibers. It has a long history as a material for writing, drawing, packaging and printing. However, with the wide concern on a sustainable and environment-friendly lifestyle, paper as a renewable and biodegradable material has attracted more attention to be designed as functional materials far beyond its conventional usages. Furthermore, the advent of paper-based microfluidic devices for medical diagnostics in the developing countries pioneered by Whitesides and his colleagues has generated a boost on the research of paper-based materials.[1] Paper as a substrate is highly promising since it is low-cost, lightweight and flexible. In order to create functions for paper materials, functional molecules including small molecules and polymers can be introduced into paper systems. Paper modification by small molecules needs the least amount of coating materials for the functionalization, and the generated layers on the paper surface are regarded as "ultra-thin" coatings. Nevertheless, the chemical and thermal stability should be considered.[2] In contrast, polymers with functional moieties can create thicker layers/higher amount of functional groups on the paper substrates. Furthermore, coatings can be designed with a higher chemical and thermal stability. Stimuli-responsive polymers with dynamically controllable sensitivities have been emerged as one of the biggest scientific interest in polymer research from both academic and industrial sides. If such polymers are used as paper coating, the properties of generated stimuli-responsive paper materials can be adjusted by external triggers, which is of great importance to be used for paper-based sensor and actuator development.

In the following chapters, various stimuli-responsive polymers will be first presented (Chapter 1.1.) followed by the introduction of stimuli-responsive paper materials (Chapter 1.2.) including structure and properties of paper substrate (Chapter 1.2.1) and stimuli-responsive polymer modified paper materials (Chapter 1.2.2). Finally, stimuli-responsive materials based on spiropyran (Chapter 1.3.) will be summarized in four parts: structure and properties of spiropyran (Chapter 1.3.1), spiropyran-functionalized polymers (Chapter 1.3.2), spiropyran-functionalized thin films (Chapter 1.3.3) and spiropyran-functionalized paper materials (Chapter 1.3.4).

1.1. Stimuli-responsive Polymers

Mother Nature always gives us highly valuable inspiration for scientific research. For example, in the face of danger, sea cucumbers can swiftly increase their stiffness by multiple magnitude for self-protection; sunflowers rotate with the direction of the sun; cuttlefishes change their skin color for camouflage or warning potential predators. Since the switching processes of these reactions are based on complex responses of biomacromolecules, scientists are motivated to design novel stimuli-responsive polymer systems which can mimic the behavior of natural creatures.[3]

Stimuli-responsive polymers are macromolecules that undergo chemical or physical changes in respose to external changes in their local environments. They can also be named as "smart" or "intelligent" polymers.[4] Such stimuli-responsive polymers can be effectively fabricated as bulk solids, gels, micelles, thin films, nanofibers, or coated on the substrates to form smart surfaces, which show a promising prospective in the applications such as sensors, actuators, smart textiles, intelligent medical instruments (controllable drug/gene delivery), artificial muscles and robotics, electrochemical devices and so on.[5–6] According to the different exterior stimuli, they can be classified to physical and chemical-responsive polymers. The physical stimuli can be for example mechanical force, electric/magnetic field, light and temperature. The chemical stimuli include electrochemical agents, pH value, ionic strength and molecules. When exposed to the corresponding stimuli, such polymers can undergo different dimensional changes depending on their original physical states as shown in Figure 1-1.[7] Nowadays, scientists make efforts to design multi-responsive and new functional polymers as well as enhance the performances of existing polymer systems to meet the need both from industry and our daily life.[8–9]

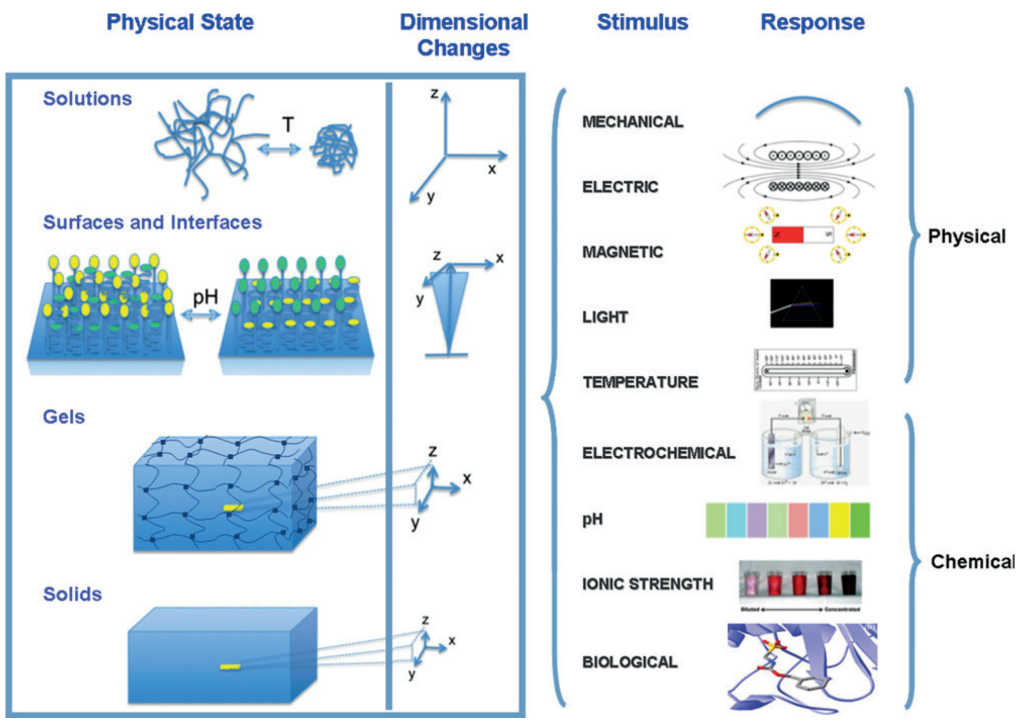

Figure 1-1: Schematic illustration of physical states of stimuli-responsive polymers and the corresponding dimensional changes by various physical and chemical stimuli.[7] (Reproduced with permission from ref 7. Copyright (2009) Elsevier).

1.2. Stimuli-responsive Paper Materials

Once stimuli-responsive polymers are being applied on surfaces, “smart” surfaces with dynamically controllable properties can be generated. Conventional substrates are glass, silicon and plastic. Another interesting material is paper which has recently attracted extensive attention due to its unique structure and properties leading to many applications in the areas of sensors and actuators.

1.2.1 Structure and Properties of Paper Substrate

Paper is made by dewatering a cellulose fiber suspension (also called pulp) which is mainly made from wood or cotton followed by filtration, pressing and drying. Figure 1-2 demonstrates the cellulose fibers in the paper made from wood cells. The length and width of cellulose fibers are normally 1–3 mm and 10–40 μm, respectively. The smaller fibrils in the cell wall are made of microfibrils with the diameter of about 3–20 nm and the most amorphous parts in between are filled with lignin and hemicelluloses. The cellulose chains in the microfibrils originate partly form crystalline regions and are connected with each other by hydrogen bonding through various hydroxyl groups. Cellulose is a polysaccharide consisting of linear chains of ß (1→4) linked D-glucose units. The average number of glucose units linked with each other is labeled as degree of polymerization. In dependence of origin and treatment, this degree of polymerization can reach from below 100 to several thousands.

Shorter fibers can decrease the pore size in paper sheets and increase the opacity, while the longer ones increase paper strength. In addition, according to different applications, additional additives such as fillers, sizing agents and pigments can be added during the paper-making processes. After dewatering, cellulose fibers form networks in the paper system, which results in a porous material with rough surface. The pore dimention is normally of 1–10 μm.[10]