

## Review

## Photomodulation of macroscopic properties

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## ABSTRACT

We review macroscopic properties of materials that can be modulated by light through switching between the two stable states of a photochromic system. In special cases, the photochromic compound is the only component of the material, but in most cases it is either embedded or covalently linked to a suitable host, which is normally a liquid crystalline phase, a glassy or a rubbery polymer, or an interface. We analyze examples that illustrate changes in refractive index, transmission of polarized light, reflectivity, light dispersion, polarization, charge transport capability, dielectrical properties, stable phase, microscopic surface relief in large areas, hydrophobicity of the surface, permeability, and even bulk mechanical deformations. The basis of such changes at a molecular level is associated with a difference in the shape, dipole moment, polarizability, or electronic features of the photochromic species, and their different interaction with the environment. In some cases, studies were performed at the single molecule level. Each effect is discussed stressing the favorable features of the particular photochromic compounds to induce the changes and its interaction with the environment that make it suitable for the appointed application.

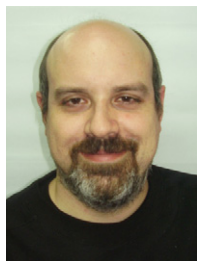
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## 1. Introduction and scope

Photochromic systems attracted attention because of their ability to exist in two distinctive states: a thermodynamically stable state and a metastable one [1]. The IUPAC criterion stresses the difference in absorption spectra between the two forms and establishes that at least one transformation must be photoinduced [2]. In practice, the transformation between the two stable states can take place very often also thermally or, less frequently, exclusively photochemically in both directions. Very importantly for the examples developed in this work, the IUPAC glossary also indicates that the transformation is accompanied by differences in other physical properties. Mainly this feature of the photochromic system is explored in what follows.

The possibility to achieve wavelength selectivity in the photoconversion as well as exclusively photochemical reaction in both ways is one of the main appealing features of photochromic systems. This allows photocontrol of the composition and, in this way, of some of the properties of the photochromic pair or those of the host material. Reversibility is also required for a functional photochromic system. Thus, the changes can be reversed, and induced again, ideally a great number of times.

Some biological signaling and light harvesting systems work on the basis of a photochromic system. This assures robust reversible cycling of the receptor system. Retinal in rhodopsin or bacteriorhodopsin [3,4], or phycocyanobilin in phytochrome [5] work as photochromic light receptors triggering information or light-to-energy storing processes in animals, plants or bacteria. The host protein, providing adequate in vivo environment for the optical, thermodynamic, and kinetic characteristics of the photochromic switching reaction, is the other key factor of the whole light-active system. Following this approach, photochromic functionalities were incorporated to the main or to the lateral chains of polymers to obtain more effective materials.

Photoswitching, photorecording, or photocontrolled data storage, are highly researched fields to which many reviews were devoted [6–11]. Light control of the state of a system allows remote and fast writing–erasing of information and with a great spatial density (regulated by diffraction limited focusing), as well as remote wireless switching. Nevertheless, optical reading of the system involves shining light on it and in this way inducing photochemical reactions that shift the system to a new photostationary state. This problem is known as destructive reading. To circumvent destructive reading two solutions were approached. A chemically inspired solution involves a coupled equilibrium of one of the components of the photochromic system, such as a redox or proton transfer process, thus yielding a more stable, photochemically inactive state, that can be probed with light without erasing risks [12]. A more physically inspired solution is based on inducing structural changes in a host material or at the macromolecular level, so that optical interrogation can still give information on the current state of a device, probing properties other than absorption. The first case is limited to special three (or more) state systems, a minority amongst the extended list of known photochromic examples and involves a great synthetic effort and the possibility of introducing secondary reactions in the whole transformation that might enhance fatigue. The second approach, on the other hand, is more general for all kind of photochromic compounds, and has the advantage of maintaining the optical probing, perhaps the most attractive way because of its favorable remote and fast characteristics. In this case, optical probing must involve wavelengths far from the photochemically active absorption bands of both isomers; i.e. longer wavelengths that allow the use of cheap NIR lasers. Refractive index, light dispersion and reflection, polarization changes, infrared absorption and Raman dispersion, are representative examples. All these examples involve the use of a probing signal which is decoupled to the photochemically active light. Also other physical properties such as electrical polarization, phase change of the host material, microscopic or macroscopic mass transport, hydrophobic or hydrophilic character, or bulk deformations were photoinduced and tested.

In materials chemistry, the host of a photochromic system for photomodulation purposes is normally a polymer or a liquid crystal. The choice depends on the particular application or goal. The favorable features of liquid crystals for these applications are their fluidity, packing ability and local order, as well as their high susceptibility to changes in the molecular characteristics of the guest and its associated changes in host–guest interactions, such as dipole moment, H-bonding, and molecular geometry or packing, “shape” in a broad sense.

Polymers enhance the processability of the system and thus facilitate the preparation of devices. They offer a more rigid environment that is unique in some applications where rigidity is searched to freeze the changes, such as in compact disks. In many cases, a combination of both, i.e. polymeric liquid crystals (PLC), in particular elastomers have been used and proved to be the better choice [13]. PLCs doped with photochromic systems have been explored to achieve devices that are electronically driven, but that can also be optically actuated.

Another important aspect in functional systems based on photochromic compounds is related to the behavior of the photoactive material towards its surrounding. As illustrative examples, the permeation of a light sensitive membrane can be switched by pore control, the surface wettability can be modulated by the change of hydrophilicity, or a neat mechanical force can be induced by physical bending of the material.

In this work, we shall review the applications of photochromic compounds concerning their ability to modulate optical properties of the system (changes in refractive index, transmission of

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