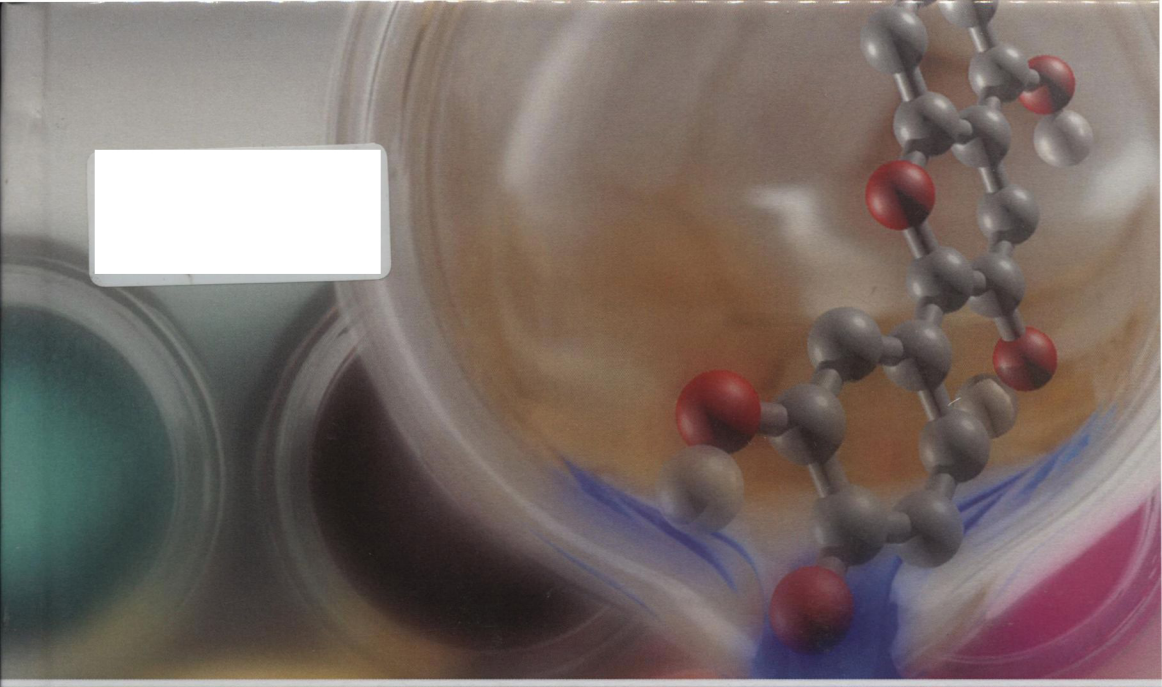

Thermochromic and Thermotropic Materials

Arno Seeboth
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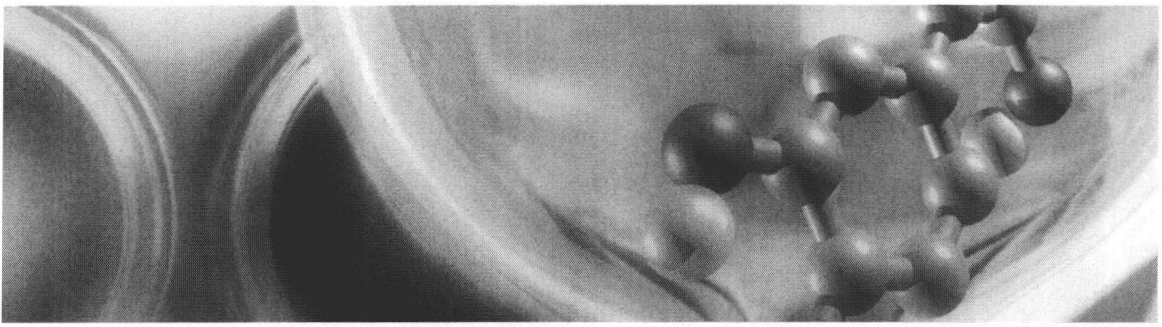

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Preface

Thermochromism denotes the change of color and thermotropism the change of transparency in dependence on temperature. Already in antiquity the color change of certain gemstones under exposure to high temperatures was known. For instance, the vermilion-red of ruby transforms into a lime green if heated to a sufficiently high temperature and returns upon cooling. The coupling of the optical appearance with an external stimulus is a material immanent sensor or actuator functionality which opens the way for novel applications with enormous economic potential.

The accelerated development of advanced materials with thermochromic properties in the recent past has led to a true renaissance of this long-known phenomenon. Although thermochromism rarely occurs it has been observed in totally different material classes and its origin is multifarious. Thermochromic materials can be monomers or polymers, organic or inorganic compounds, single-component or multi-component systems. The optical appearance can change abruptly or continuously with temperature, reversible or irreversible, and can be due to changes of the light reflection, absorption or scattering properties.

The present book is focused on all kinds of thermochromic and thermotropic materials and on the mechanisms which trigger their optical properties. A selected set of representative publications on this topic is evaluated. Chapters 1–3 give an overview on the origin of thermochromism and thermotropism in the various material classes using typical examples. This part is structured in the first level according to the way the materials interact with light and in the second level according to the different material classes.

Chapter 1 reports on materials whose light reflection properties change with temperature. These comprise liquid crystals, crystalline colloidal arrays and materials exhibiting semiconductor to metal transitions. The periodic supermolecular ordered structure of liquid crystals and crystalline colloidal arrays can lead to physical

coloration by the reflection of light. Thermochromic effects occur in these materials due to changes in the periodicity of the supermolecular structures with temperature. A semiconductor to metal transition is another effect leading to changes of the reflection properties with temperature.

Materials with temperature-dependent light absorption properties in the visible range are summarized in chapter 2. Transitions between crystal modifications of gemstones and other inorganic solids as well as conformational changes in overcrowded ethenes and conjugated polymers are discussed. The shift of the chemical equilibrium of the formation of colored complexes or between different structures of functional dyes in specific composites and surface plasmon resonance effects of nanoparticles are also parts of this chapter.

In chapter 3 materials changing their light scattering properties with temperature, resulting in a transition between clear, transparent and opaque light scattering state, are presented. Some authors denote these materials as thermotropic, others as thermochromic. Since no color changes take place, the term thermotropic will here be used for these materials and the term thermochromic will be only used in the proper meaning of the word restricted to temperature-dependent color effects. Phase separation processes, aggregation effects, the appearance of liquid crystalline phases or a different temperature dependence of the refractive indexes of a domain and a matrix material can be the origin of the thermotropic switching effect. Thermochromic and thermotropic effects are of course not mutually exclusive and can both appear parallel in one material.

The application-oriented development of tailored thermochromic and thermotropic materials is reviewed in chapter 4. Thermopaper, temperature sensing labels, coatings, packaging and plastic articles, as well as tunable light filters place a set of different demands on the material properties. The states of the art of either already existing or potential future applications is discussed with a special focus on energy-efficient smart windows.

In chapter 5 are the active triggering and the energetic characterization of thermotropic materials reported. The active triggering of the switching of thermochromic or thermotropic materials forms the basis for display applications.

Finally, concluding remarks are made in chapter 6. The development of novel multifunctional materials combining, for example, thermochromic or thermotropic effects with an additionally chromogenic behavior is motivated.

Arno Seeboth
Detlef Lötzsch

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Chapter 1

Thermochromic Materials Based on Reflection

1.1 Light Reflection

Light reflection is a redirection of light. Common examples include the reflection of an image by a mirror or by a smooth water surface. The direction of the reflected light is determined by the laws of reflection as following. Incident and reflected light beams as well as the normal of the reflecting interface at the point of incident are in one plane. The angle between incident light beam and layer normal is the same as the angle between reflected light beam and layer normal but both are on opposite sides of the layer normal. Smooth interfaces lead to specular (mirror-like) reflection while rough interfaces like in polycrystalline materials lead to diffuse reflection.

Light reflection occurs at the interface between two media, air and matter. For non-absorbing media the reflectance (R) at normal incident can be calculated according to Eq. (1.1) in which n_A and n_B stand for the respective refractive index of medium A and B.

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$$R = [(n_A - n_B)/(n_A + n_B)]^2 \tag{1.1}$$

For absorbing media the refractive index becomes complex. The reflectance of metals or other absorbing media at normal incident is given by Eq. (1.2) in which n_A and k_A stand for the real and the imaginary parts of the complex refractive index of the absorbing medium A.

$$R = [(n_A - n_B)^2 + k_A^2]/[(n_A + n_B)^2 + k_A^2] \tag{1.2}$$

Metals in general exhibit high reflectance due to scattering of almost free electrons. At normal incident the reflectance can reach values close to 100%. For example, the reflectance of silver is about 96%. A semiconductor to metal transition is accompanied by large changes of the reflectance and thus such materials are thermochromic (Section 1.4).

The reflection of light by materials having periodical structures can give rise to the appearance of physical colors. This so-called Bragg reflection named after its discoverers William Lawrence Bragg and William Henry Bragg occurs if the reflections of the numerous planes of the periodical structure interfere constructively, which is the case when the wavelength of the incident light or a multiple of it fits with the spacing between the planes. Accordingly, depending on the layer spacing, specific light wavelengths are selectively reflected. This behavior is expressed by Bragg's law (1.3).

$$m\lambda = 2nd \sin\theta \tag{1.3}$$

In (1.3) m stands for the order of diffraction, λ for the wavelength of the incident light, n for the refractive index of the material, d for the interplanar spacing and θ for the angle between the incident light and the diffracting planes.

Physical colors are observed if a light wavelength of the visible range is selectively reflected. An additional change of the layer spacing with temperature results in thermochromism. This can take place in liquid crystals (Section 1.2) or crystalline colloidal arrays (Section 1.3).

Since the Bragg reflection wavelength depends on the angle between the incident light and the diffracting planes, the observed physical color varies with θ. When the angle of the incident light

shifts from normal to oblique, the selective reflection shifts to shorter wavelength.

1.2 Liquid Crystals

Several compounds with a form anisotropic molecular structure do not directly transform from the solid crystalline into the isotropic liquid phase, but exhibit one or more so-called liquid crystalline phases in between. Liquid crystalline phases can flow like fluids. Otherwise, the molecules still have a long-range orientational order and thus these phases possess anisotropic physical properties like solids.

Until today more than 80,000 organic compounds are known to possess liquid crystalline phases [1]. The form anisotropy of the molecules can be a rod-like (length/diameter > 3), disk-like (thickness/diameter < 0.3), pyramidal or banana-shaped structure. The formation of ordered structures by highly form-anisotropic molecules can be understood in terms of steric constraints that occur on filling space.

If the liquid crystalline compound itself has a chiral structure or a chiral compound is added, a helical superstructure appears in certain liquid crystalline phases. The helical structure can be left-handed or right-handed and its pitch can range between about 100 nm and infinite. Whereas one enantiomer produces a left-handed helix, its mirror image structure will cause the formation of a right-handed helix. The length of the helical pitch depends on the molecular structure and concentration of the chiral compound, on the phase type and on temperature. Since the helix represents a long-range periodic structure, incident light satisfying the Bragg conditions is selectively reflected. Frequently, the wavelength of the reflected light corresponds with the visible range, leading to the appearance of brilliant colors and due to the temperature dependence of the pitch length to thermochromic properties.

1.2.1 Cholesteric Liquid Crystals

The cholesteric phase is the chiral form of the nematic phase. Figure 1.1 displays the structures of both phases on the example of rod-like and disc-like molecules.

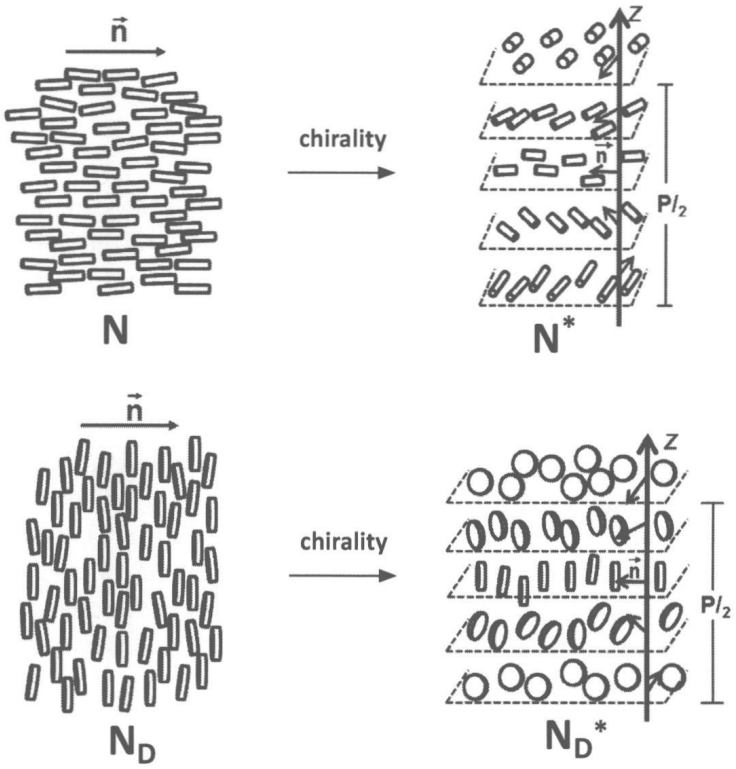

Figure 1.1 Structure of the nematic (left) and of the cholesteric (right) phases of rod-like (top) as well as of disk-like molecules (bottom).

In the cholesteric and in the nematic phase, the molecules have a long-range orientational order without any positional order. The orientational order is characterized by the order parameter *S*.

$$S = \tfrac{1}{2} \langle 3 \cos^2\theta - 1 \rangle \tag{1.4}$$

In (1.4) θ stands for the angle between the orientation of a single molecule and the mean orientation of the liquid crystalline phase, which is described by the director *n*. The brackets denote that an average over all molecules in the sample is calculated. Order parameters of liquid crystalline phases typically range between 0.3 and 0.9.

The only structural difference between the nematic and the cholesteric phase is the helical superstructure of the cholesteric

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