Mini-review

Received: 26 June 2012 Revised: 2 August 2012 Accepted: 15 September 2012 Published online in Wiley Online Library:

(wileyonlinelibrary.com) DOI 10.1002/pi.4395

The unique optical behaviour of bio-related materials with organic chromophores

Francesco Ciardelli,[a,b]* Monica Bertoldo,[b] Simona Bronco,[b] Andrea Pucci,[b,c] Giacomo Ruggeri[b,c] and Francesca Signori[b,c]

Abstract

Molecularly designed materials based on macromolecules and organic dyes offer unique opportunities in connection with the possibility of preparing optically responsive 'smart' materials. Indeed macromolecules are able to transmit and amplify small signals reaching sites at interacting distance through the involvement of the whole chain. The corresponding materials can then acquire stimuli-responsive properties in relation to specific features connected to primary structure and conformation. As a first approach to benefit from the above features for preparing eco-compatible smart materials, bio-related polypeptides, polysaccharides and polyesters can be used as the macromolecular partner in combination with a selected dye following different interaction methodologies. Two distinct routes were used to prepare optically responsive products from the above bio-related polymers, respectively based either on the covalent bonding to the original macromolecules of photochromic molecular species, such as azobenzene and spiropyran, or on the morphology-modulated dispersion of highly conjugated dyes in the polymer bulk. Examples related to the two different routes have been investigated in our laboratory and are presented and discussed also with reference to selected recent cases from the literature.

Keywords: organic chromophores; bio-related polymers; photoresponsive organic materials; colour change; optical traceability

INTRODUCTION

Bio-related polymers have attracted increasing interest in recent times with the aim of producing materials characterized by a low environmental impact and originated from renewable, non-fossil sources. In addition, biopolymers often have more sophisticated functional properties related to their peculiar sensitivity to the environment, thus assuming a highly selective and, in particular, stereoselective behaviour which is accompanied by easily detectable optical and chiroptical responses. For these reasons, bio-related polymers are an excellent starting basis for preparing smart responsive organic materials according to a number of different approaches and in order to respond to the needs of various applications.

Nature has produced a large amount of biomacromolecules containing chromophores for various objectives. Typical examples relate to proteins involved in vision and the entrapping of solar light for the purposes of life in animals and plants.[1–5]

Within such a fascinating frame, the present paper focuses on examples demonstrating the use of polypeptides, polysaccharides and bio-related polyesters as amplifiers of the optical response of light-responsive units (chromophores) contained within them. In the examples discussed, the chromophore can be either covalently bound to or simply dispersed in the bio-related polymer. These bi-component tools (macromolecule + chromophore), which act as responsive materials upon a specific external light stimulus, can work as active units for sensing, tracking and identification purposes, as well as for information storage.[6,7]

Many different routes to reach these goals are in principle possible, also with reference to the various parameters which can govern the resulting performances. Molecular structure of both macromolecule and chromophore clearly plays a fundamental role, but for each combination additional parameters, such as composition, binding interactions, morphology and sample history, can also markedly affect the response, which will be in any case additionally dependent on the environment in which the system is acting.[8] A complete coverage of the topic is out of the scope of this paper. Rather, the main objective is to provide some clear concepts of the basic factors related to the binding and non-binding interactions between the macromolecule matrix and the light-absorbing species.

Accordingly, the present mini-review is mainly focused on the optical behaviour of bi-component systems, based on a bio-related polymer matrix (polypeptides, polysaccharides and polyesters) having a chromophore (light-responsive unit) either covalently bound to the macromolecules or simply molecularly dispersed in the bulk. The examples here reported come predominantly from the work performed in the authors' laboratories, with complementary additional examples selected

* *Correspondence to: Francesco Ciardelli, SPIN-PET, Spin-off Company of the University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy. e-mail: fciard@dcci.unipi.it*

a *SPIN-PET, Spin-off Company of the University of Pisa, Via Risorgimento 35, 56126, Pisa, Italy*

b *Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche (IPCF-CNR), Area della Ricerca, Via G Moruzzi 1, 56124, Pisa, Italy*

c *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italy*

Francesco Ciardelli was full Professor of Polymer Science at the University of Pisa from 1975 to 2010. Presently he is President of SPIN-PET srl, a spin-off Company of the University of Pisa for technology transfer in the Tuscany industrial area of Pontedera. He obtained his PhD at the University of Pisa with Professor Piero Pino and was post-doc and visiting Professor at UCL-London, MPI-Muelheim,UNICAL-Berkeley, Kyoto University, ETH-Zurich and University Paris-VI.

Dr. Monica Bertoldo studied Chemistry at the University of Ferrara. She received her Ph.D in Material Science from the Scuola Normale Superiore of Pisa in 2003. Currently she's researcher at the Institute for Chemical-Physical Processes of CNR at Pisa. Her main research interests includes modification of natural polymer, polymer surface and preparation of polymer nanoparticles. In addition she's also interested on physical properties of polymers at interfaces.

Simona Bronco was Researcher at Istituto Nazionale per la Fisica della Materia from 1999 to 2010. Presently is Reasercher at the Istituto per i Processi Chimico-Fisici (IPCF) of Consiglio Nazionale delle Ricerche (CNR) in Pisa. She obtained her PhD at Swiss Federal Institute of Technology in Zuerich (Switzeland) with Prof. Giambattista Consiglio on the study of the influence of the catalytic system used in the regio- and stereochemistry control of the CO-Propylene copolymerization. She has over 15 years international experience in polymer science including interphase investigation and modulation, polymer blends and composites preparation, plasticity tuning and compatibilization of biodegradabile and compostable polymers.

Andrea Pucci received his M.S. degree in Chemistry (1999) and his Ph.D. (2003) in Chemical Science from the University of Pisa. In 2011 he joined the University of Pisa as an assistant professor. He was visiting scientist at ETH in Zurich, at CBMM of the Polish Academy of Science and at University of Manchester. His research interests focus on the preparation of field responsive thermoplastic materials, polymers for fuel cells and for lubricants.

Giacomo Ruggeri received his M.S. degree in Industrial Chemistry (1977) at the University of Pisa where is currently associate professor of Industrial Chemistry. He was a visiting scientist at the PSE, University of Massachussetts, Amherst, at the IQ de la Universidad Central de Venezuela, Caracas and at the IQ, Universidade Estadual de Campinas, Sao Paulo, Brazil. His scientific interests mainly concern the field of electro-optical responsive polymeric nanomaterials.

Francesca Signori received her Master Thesis in Polymer Science in 1999 (University of Pisa) and her Ph.D. in Biomaterials in 2003 (University of Trento). In 2006 She was one of the the recipients of the European Biomaterials and Tissue Engineering Doctoral Award *(EBTEDA)* by the European Society for Biomaterials. She was visiting scientist at Twente University (The Netherlands) in 2002 and 2011. Her scientific activity focused on polymer science and technology, mainly on the synthesis and modification of biodegradable thermoplastic materials, in the perspective of biomedical and industrial applications. She is also active in the preparation and investigation of biodegradable polymer based composites and blends.

from the recent relevant literature, on the basis of the evidence provided by the results about the capacity of the matrix to amplify the chromophore optical response, both in homogeneous and in polyphase systems. Homogeneous systems are typically represented by covalently bound biomacromolecule and chromophore, while polyphase systems are normally observed when the chromophore is molecularly dispersed in the polymer matrix. Moreover, the specific interactions occurring between the biomacromolecule and the chromophore tune the optical behaviour of the latter, by means of geometrical assemblies driven to exciton coupling and self-organization. The resulting distinct optical behaviour with innovative characteristics and responsive character upon application of external stimuli are then generated by the synergic interaction with the polymer structure and system dynamic.

Finally, the objective of this mini-review is to relate molecular parameters to final optical response through the understanding of the effective interactions among the different components. Therefore, the following sections are organized on the basis of a molecular descriptive approach by reporting selected examples and their optical behaviour in two separate sections. The first is devoted to polypeptides and polysaccharides with covalently bound photochromic groups acting as triggers for the light-induced event. The second is devoted to bio-related polymers with a dispersed dye which show optical response under mechanical and thermal stimuli affecting the whole blend.

BIO-RELATED POLYMERS WITH COVALENTLY BOUND ORGANIC CHROMOPHORES

Polypeptides

Photoresponsive polypeptides are prepared by bonding photochromic units to poly(L-α-amino acid) macromolecules.[1] These systems are characterized by the presence of two

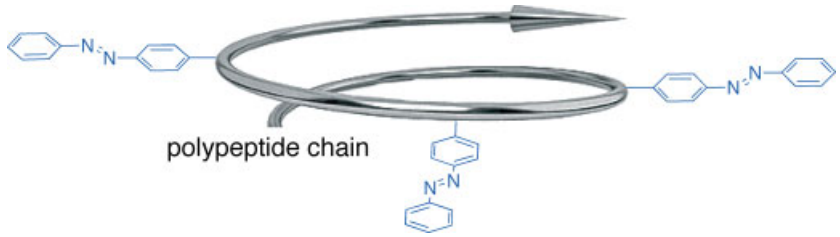


Figure 1. Distinct chromophores in photoswitchable azo-modified poly(L-α-amino acid)s: polypeptide main-chain in the 180–210 nm range; azobenzene side-chain in the 250–400 nm range.

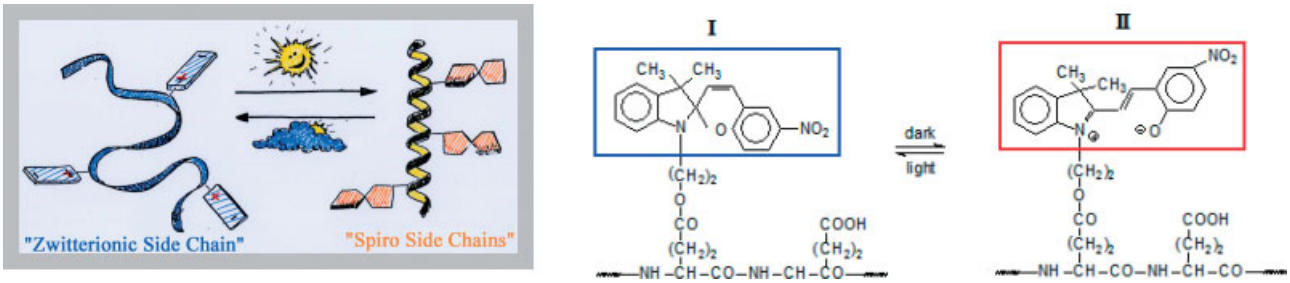


Figure 2. Helix–coil photomodulated response of spiropyran-modified poly(glutamic acid).[17]

distinct chromophores, the main-chain peptide and the side-chain azobenzene group, absorbing in separate spectral regions thus allowing independent photostimulation and detection of response (Fig. 1).

Within this category, poly(L-glutamic acid) containing about 30 mol% azobenzene units adopts a β-structure at a pH below 5 which is not affected by light irradiation in the side-chain absorbing region, in spite of the *trans* to *cis* isomerization of the azobenzene groups. An increase in pH to 7 induces the transition of the polypeptide to the random coil conformation, also not affected by the photoisomerization of the azo side-chains. However, at pH values in the range 5–7 (close to the p*K* of the conformational transition), irradiation causes a marked decrease of the ordered structure which is completely reversed in the dark.[9] Moreover the same poly(L-glutamic acid) with 4-aminoazobenzene-4-sulfonic acid sodium salt containing a very low amount (1.9%) of azobenzene sulfonate units showed a pH-dependent α-helix–coil transition, while a polypeptide containing 46 mol% azo units had a random coil conformation at any pH. The UV light-induced *trans* to *cis* isomerization of the azo units did not induce any conformational changes for either of the polypeptides at any pH. By contrast, a polypeptide containing 9.3 mol% azobenzene sulfonate units at pH = 4.3 exhibited, on irradiation in the azobenzene region, a variation of the circular dichroism (CD) spectrum corresponding to a decrease in the α-helical structure from 96 to 45%. The replacement of the carboxylic side-chains as in poly(glutamic acid) with amino side-chains as in poly(L-lysine) gave substantial changes in the photoinduced conformational response. Indeed azobenzensulfonyl-modified poly(L-lysine) had a random coil conformation in pure hexafluoro-2-propanol (HFP), independent of the *trans–cis* photoisomerization of the azo units. Reversible variations of the helical content were observed by alternate illumination at 340 and 417 nm after addition of methanol from 2 to 15%, thus providing a clear example of a *gated photoresponse*.[10]

Poly(L-aspartate)s adopt helical structures of both left-handed and right-handed screw senses, depending on the chemical structure of the ester group in the side-chains.[11] Moreover in poly(β-benzyl-L-aspartate), the presence of substituents such as chloro, methyl or nitro groups on the benzyl ring provides helical polypeptides that can adopt the left-handed or right-handed sense depending on the position of the substituent.[12–14]

An azo-modified elastin-like polypeptide exhibits a so-called 'inverse temperature transition': the compound gives crosslinked gels that remain swollen in water at temperatures below 25 °C but deswell and contract with a rise in temperature. The *trans–cis* photoisomerization of the azo units, obtained by alternate irradiation at 350 and 450 nm, allows the photomodulation of the inverse temperature transition. This result indicates that attachment of a small amount of azobenzene chromophores is sufficient to render photoresponsive the inverse temperature transition of elastin-like polypeptides and provides a route to protein-based polymeric materials capable of photomechanical transduction.[15]

Poly(L-glutamic acid) with more than 80% azobenzene side-chains undergoes photoinduced aggregation–disaggregation processes together with the occurrence of large photosolubility effects. In the dark this polymer was soluble in HFP in the α-helix structure; formation of aggregates occurred on addition of a small amount of water (15% by volume) to the HFP solution followed by the total and quantitative precipitation of the polymer as a yellow material. Irradiation of the suspension for a few seconds at 350 nm caused the complete dissolution of the polymer, the solubility depending on the *cis–trans* isomeric composition of the azobenzene side-chains.[16]

Additional effects were observed with spiropyran as protochromic side-chain, because of the marked structural changes induced by visible light irradiation in connection with the polarity of the medium.[17] HFP solution of poly(L-glutamate)s containing various amounts of spiropyran units are dark coloured, as spiropyran assumes in this polar solvent the conjugated merocyanine form. Complete bleaching of the colour occurred on exposure to sunlight due to the formation of the spiro form. Notably the light irradiation produced the parallel coil to α-helix conformational transition (Fig. 2). The original colour and conformation were restored by switching off the light.[17,18]

The effect of charged species formation and disruption by light irradiation was used for amphiphilic block copolymers decorated with photochromic groups.[19] Accordingly micelles of a photosensitive amphiphilic diblock copolymer in aqueous solution could be partially disrupted and regenerated by UV and visible light irradiation, respectively.[20] Along the same lines, diblock copolymers showed in aqueous solution a reversible double-responsive micelle formation on exposure to UV light at 30 °C or at 15 °C under visible light, thus providing a photo- and thermoresponsive system.[21] In a recent study, spiropyran-modified polypeptide block copolymers were described, undergoing a complete reversible micellar transition with aggregation–dissolution–aggregation in water solutions under light irradiation, accompanied by a moderate reversible variation of the α-helix content. The possible effect of charged groups on polymer structure was indicated, thus confirming that both hydrophobicity and secondary structure contribute to the shape of the final aggregates.[22] A similar effect was observed in analogous polymers of L-lysine where the lack of light-induced conformational changes was attributed to the extended coil conformation adopted by the polycation, which is formed by protonation of the unmodified lysine side-chains by the acid solvent HFP.[23] The system responded again to light irradiation, giving coil to α-helix conformational changes, after the addition of appropriate amounts of triethylamine to the HFP solution.[24] This provides an additional example of a *gated photoresponse*, as exposure to light and darkness conditions produces reversible photoinduced conformational changes in a defined solvent composition range.

A spiropyran-modified bioelastic polypeptide obtained from elastin responding to sunlight–darkness cycles or, alternatively, sunlight–UV cycles provided a route to photoresponsive materials capable of photomechanical transduction without the need of either solvents other than water or UV irradiation, and with a high efficiency.[25]

Molecular recognition-based logic gates activated by chemicals[26] were developed by preparing a tandem protein kinase substrate peptide composed of two different kinase substrate regions joined in series and a spiropyran derivative at the *N*-terminus as the gate molecule. Information was recorded onto the gate molecule by protein kinases, stored stably as phosphoesters, read based on the extent of the spiropyran-to-merocyanine thermocoloration, and erased by phosphatase-catalysed dephosphorylation, resulting in the gate molecule being reset to the initial recordable state.[27]

A summary of the results shows then how the photoisomerization of different photochromic groups attached to polypeptides can produce 'order ↔ disorder' conformational changes, which, such as random coil ↔ α-helix, take place as highly cooperative transitions. In these systems, photochromic polypeptides act as amplifiers and transducers of the primary photochemical events occurring in the photoresponsive side-chains in combination with the environmental effects here simulated by solvents with variable polarity. The structure and properties of the complex systems can then be reversibly modulated (Fig. 3).

These results are of utility for studying complex biopolymer systems. Protein folding is today one of the most studied aspects using the approach presented above which helps to reduce the gap between the information held in the genetic sequence and protein structure. During the folding process, ultrafast rotations occur around single bonds on the picosecond timescale, whereas the formation of secondary structures and their

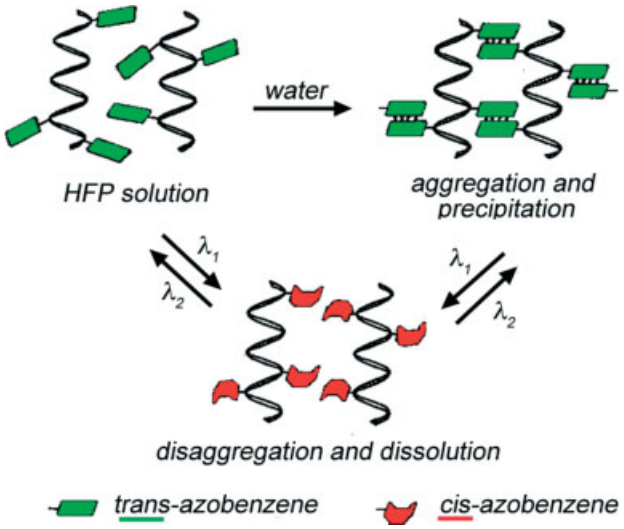


Figure 3. Light- and solvent-induced effects on conformation and supramolecular interactions of polypeptides with photochromic azobenzene side-chains.

rearrangement occur on the microsecond to second timescale.[28] Dynamics of tertiary and quaternary structures extends from milliseconds to seconds and even longer. Conformational transitions of peptides and proteins are most commonly triggered by changing the environment of the molecule, thereby shifting the equilibrium constant of the process under investigation. Among these methods, laser-, pH- and temperature-induced jump experiments have been shown to allow for sub-nanosecond time resolution.[29–32] Even faster triggering with a possible sub-picosecond time resolution can only be achieved with a molecular switch incorporated in the peptide chain. Ultrafast light-induced changes of the switching molecule initiate structural dynamics of the peptide on the picosecond timescale by changing a conformational restraint. The design of peptides with built-in chromophores that enable fast conformational changes by irradiation with monochromatic light is a particularly powerful approach for investigating structural transitions during protein folding.[33] These systems are bistable, i.e. sufficiently long lived in both isomeric forms and small enough to resolve changes in secondary structure using spectroscopic techniques including CD, NMR and ultrafast optical spectroscopy experiments.

Polysaccharides

Various chromophores have been linked to polysaccharides through covalent bonding for a variety of objectives, particularly probes, sensors and sensitizers.[34] The synthetic strategies were based mainly on esterification, etherification, oxidation and, more recently, 'click' methods.[35–42] Here, the focus is on materials where the behaviour of the chromophore is affected by the organization driven by the polysaccharide structure and, conversely, the photoresponse of the chromophore affects the polysaccharide organization.

In this connection the optical behaviour of regioselectively functionalized *O*-methylcellulose derivatives with 9-butyl-9H-carbazole in the C6 position (derivative A in Fig. 4) or C2–C3 position (derivative B in Fig. 4) were compared. Both C6- and C2–C3-functionalized celluloses showed photoluminescence (PL) spectra due to the emission from the carbazole unit. The emission intensity was higher for the C6 derivative and lower for the C2–C3

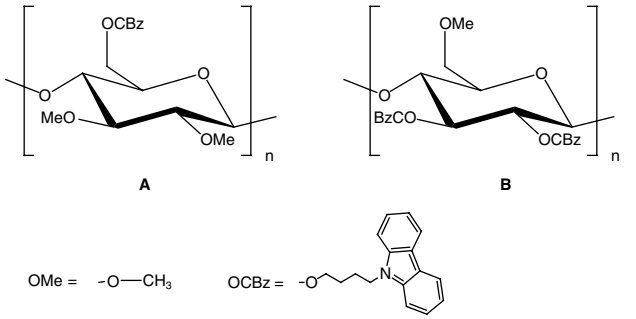


Figure 4. Structures of 2,3-di-*O*-methyl-6-*O*-(4-butyl)carbazolcellulose (A) and 2,3-di-*O*-(4-butyl)carbazol-6-*O*-methylcellulose (B).

derivative with respect to a reference poly(vinyl carbazole) (PVK), while the corresponding UV-visible absorption spectra were all comparable. Carbazole moieties covalently bonded to cellulose in the C6 position are kept isolated from each other due to the maximized spatial distance and the high rigidity of the cellulose backbone. This organization in the C6-functionalized material resulted in organic light-emitting and memory devices with superior performance compared to corresponding devices obtained with PVK or cellulose functionalized at the C2–C3 position.[43,44]

Cellulose was also reported to direct the organization of bonded porphyrin groups. In this case the efficiency was slightly lower than with carbazole, most likely because porphyrins are bulkier and can also interact with each other at a distance of two glucosidic units. Similarly to carbazole, porphyrin was better dispersed when it was regioselectively bonded to cellulose at the C6 instead of the C2–C3 position.[45–48] In addition, evidence of the templating effect of cellulose to drive porphyrin organization into a helical chiral form came from the intense bisignate Cotton effect ($\lambda_{max} = 424$ nm) of 2,3-*O*-methyl-6-*O*-porphyrinylcellulose, its negative sign indicating a left-handed helical conformation. The strongly negative CD peak in the neutral state was found to vanish completely on oxidation of porphyrin to its radical cation and to reappear on reduction. This well-defined electrochromism behaviour suggested this material as suitable for application in devices for chiroptical read-out of an electrochemically induced information input.[46]

Spiropyran-functionalized dextran exhibited reversible photoinduced phase separation in water due to the strong change of polarity of the chromophore upon irradiation.[49] Inverse photochromism was observed in acid water due to the stabilization of the open merocyanine form by protonation (Fig. 5). This latter formed under UV light irradiation and reverted back to the spiropyran form on irradiation with visible light or on heating. Under neutral pH, no merocyanine stabilization occurred and, accordingly, the polysaccharide coagulated as a result of the hydrophobization by the spiropyran moieties.[49]

Irradiation with blue light at room temperature under acid conditions converted merocyanine to spiropyran in 15 min. In the presence of poly(ethylene glycol) (PEG) a stable turbid suspension was formed since closure of the ring induces desolvation and precipitation. Next, when the phase-separated solution was heated to 50 °C, it changed to a colourless transparent solution (single-phase composition) within several minutes. The rise in temperature could be tuned in the 15–45 °C range by adjusting the PEG concentration between 6 and 7% by weight.[49]

Azobenzene moieties covalently bonded to methylcellulose provide solubility variation to the functionalized polysaccharide

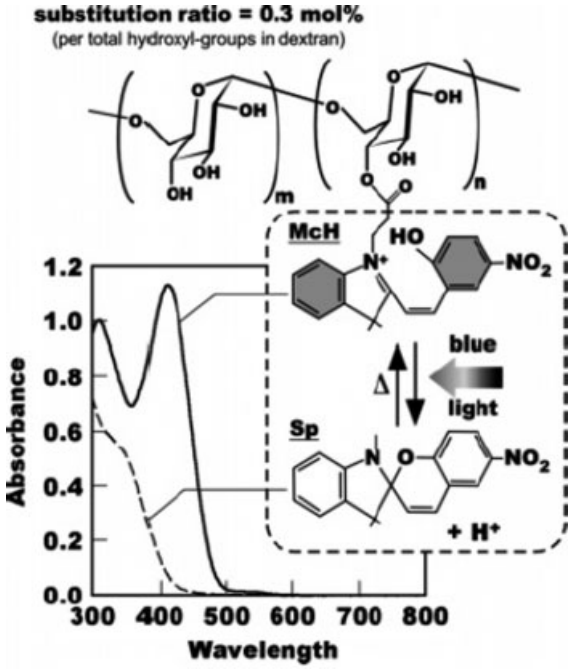


Figure 5. Chemical structure of spiropyran-functionalized dextran and the photoisomerization scheme of a 6-nitrospiropyran (NSP) chromophore. Sp, spiropyran form; McH, protonated merocyanine form. Also shown are the absorption spectra of 0.30% w/w NSP–dextran in 3.0 mmol L^{-1} HCl aqueous solution at 25 °C: solid curve, result of measurements of the sample prior to irradiation; dashed curve, result of measurements conducted immediately after sample irradiation with blue light (436 nm). (Reproduced with permission from Edahiro *et al*.[49])

as in the case of spiropyran, but the change is less distinct.[50] The difference can be explained by the stronger change of spiropyran polarity on irradiation compared to azo dyes due to the formation of a zwitterionic species in the former case.[51,52]

The structure of polysaccharides is characterized by a rigid backbone and three side sites for functionalization providing different mobility: higher at the C6 position and lower at the C2 and C3. This peculiarity seems effective in stabilizing the less stable form of the photochromic species without avoiding their photoisomerization. Accordingly, spiropyran moieties covalently bonded to any hydroxyl group of methylcellulose or cellulose acetate underwent reversible isomerization under irradiation with UV light and subsequently with visible light, but the open merocyanine form, which is the less stable form with the celluloses used, was stabilized and lasted for 1–2 h in solid films.[53,54] The formation of the zwitterionic merocyanine gives rise to well-detectable and reversible wettability increase of the cellulose films as revealed by contact angle measurements.[54] In the same way, the possibility to better accommodate the open merocyanine in a stabilized spatial geometry, because of the mobility at the C6 position, provided extremely high stability (more than two months at room temperature) to the coloured form of solid films of phthaloylchitosan regioselectively functionalized at the C6 position with spiropyran moieties.[55]

Slow thermal recovery of the most stable *trans* isomer form, after population of the less stable *cis* state, was also observed in photochromic cellulose bearing 4-cyanophenylazophenol covalently bonded prevalently at the C6 position under Mitsunobu reaction conditions.[56] The thermal recovery of the most stable isomer took two days in the dark and exhibited a two-mode

decay as for spiropyran-functionalized phthaloylchitosan.[55] The first mode was a fast process due to relaxation of chromophores trapped in a strain conformation at temperatures below the glass transition temperature. The second mode was a slow process following a single exponential decay, responsible for the unexpected high stability of the less stable form of the photochromic moiety (merocyanine and *cis* isomer).[56]

Biodegradable polyesters

Labelled polymers were used to investigate the degradation behaviour of biodegradable polyesters,[57,58] to develop optical sensor elements[59] as well as functional aggregates,[60] and to modulate material thermomechanical behaviour through controlled crosslinking.[61–63] Only a few examples are reported in the literature in which biodegradable polyesters, either from renewable resources (such as poly(lactic acid), PLA) or from oil-derived monomers (such as poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL), etc.), chemically bonded to a chromophore, were built up to afford responsive materials upon a physical (mainly UV light) stimulus.

Difluoroboron dibenzoylmethane (BF2dbn)-functionalized PCL and PLA, as well as BF2dbn-functionalized PCL–PLA block copolymers for comparison, were prepared to investigate the fluorophore response upon UV irradiation. Interestingly, while all materials in the form of solutions and films exhibited nearly identical blue fluorescence, no room temperature phosphorescence (RTP) was noted for BF2dbn–PCL films, as showed by BF2dbn–PLA films. Significantly, RTP was also observed in BF2dbn–PCL–PLA block copolymers in the solid state. Normally, RTP is enhanced in rigid matrices because of restricted degrees of freedom and thus fewer thermal decay pathways for the dye. For boron dyes in PCL, data suggested that the dye chain ends may be functioning as impurities that are excluded from polymer crystalline regions; instead, they may be concentrated in the amorphous regions between crystalline domains, where microcavities and greater free volume provide additional degrees of freedom for the dye. When PLA or poly(L-lactic acid) (PLLA) segments are grown from BF2dbmPCL macroinitiators, however, the RTP is restored for the resulting block copolymer products. Both RTP intensities and lifetimes increased with longer PLA or PLLA segments, and stronger RTP was observed for the less crystalline PCL–PLA copolymer.[64]

PCL–PEG-based polymersomes were rendered susceptible to UV-induced degradation by an incorporated 2-nitrophenylalanine group as the amino acidic joint of the two blocks. Upon UV irradiation, polymersomes undergo progressive PCL–PEG cleavage, resulting in PEG solubilization in water, thus altering polymersome aggregation behaviour/solubility in water and therefore triggering polymersome gradual collapse, due to the insolubility of PCL segments in water.[65]

PLLA as an alternative transparent matrix to poly(methyl methacrylate) (PMMA) was tested for use in luminescent solar concentrators. Indeed, low-molecular-weight PLLA films, chemically modified or blended with oligothiophene luminescence dye (T_5OH), showed excellent processability and photostability, and exhibited fluorescence quantum yields (of about 35%) even higher than that of T_5OH-doped PMMA.[66]

As previously reported for protein-based responsive materials (discussed above), many examples refer to the *cis–trans* isomerization of azobenzene derivatives chemically bonded to biodegradable polyester matrices. Indeed, azobenzene moieties undergo a light-driven inter-conversion between low-energy *trans* and higher energy *cis* isomeric states with a high degree of efficiency and without any competing side reactions. Significantly, *trans–cis* isomerization of the azo chromophore acts on and strongly modifies the chiroptical properties of the polymer matrix to which the azobenzene chromophore is bonded. In this context polylactide-*block*-polyglycidol-*block*-poly(ethylene oxide) triblock copolymers carrying 4-(phenylazo)phenyl as substituent in the polyglycidol units were synthesized. They form nanoaggregates in water, mainly used as drug delivery systems. Upon UV irradiation, the *cis–trans* conformational change of 4-(phenylazo)phenyl groups was exploited to modulate the stability of the nanoaggregates in water. Indeed, the change from *trans* to *cis* conformation of 4-(phenylazo)phenyl labels upon UV irradiation affected the critical aggregation concentration of the material in water, which was significantly higher for the *cis* conformer. More recently, PCL was also modified with light-responsive azobenzene (BP-azo), and various noanofibrous materials having increasing concentration of BP-azo tethered to PCL were produced by electospinning. The well-known *trans–cis* isomerization of azobenzene under the trigger of light at different wavelengths caused a significant change of the dipole moment and subsequently of the surface free energy. The fibres exhibited large, reversible and light-responsive wettability changes, making them interesting materials in drug delivery, tissue engineering, sensors and optical storage applications.[67]

DYES DISPERSED IN BIO-RELATED POLYMERS

Polypeptides

In most responsive, bi-component (protein + chromophore) optical tools, the chromophore is covalently bound to the protein (discussed above). It is likely that the polypeptide acts indeed as an efficient amplifier of the conformation change of the chromophore, once the external stimulus has occurred, only if the chromophore itself occupies a specific position along the polypeptide chain. Generally speaking, in these cases, an external stimulus, such as light of a selected wavelength, activates the responsive behaviour of the chromophore, resulting in a complex structural change which involves not only the chromophore itself, but also propagates to the whole protein chain.[68,69] As a consequence, protein behaviour (in terms of transport properties,[70] cell adhesion[71] and reactivity[72]) can be modulated, or switched between active and non-active states.

To the best of our knowledge, very few examples have been reported of bi-component systems designed as responsive optical tools, in which the light-responsive moiety (chromophore) is molecularly dispersed in and not covalently bound to the biomacromolecule (polypeptide or protein material). Indeed, in most of these bi-component systems, the chromophore acts as a molecular probe that selectively binds a specific biological moiety and allows its detection and the analysis of its structural properties. In these cases, the polypeptide acts as a template, and drives a structural rearrangement of the dye (conformational change, chiral aggregation), which significantly modifies the optical response of the dye. A typical example of this class of systems is the selective dispersion of thioflavin-T (ThT) into amyloid fibrils. Since its first description in 1959, the fluorescent dye ThT has become among the most widely used 'gold standards' for selectively staining and identifying amyloid fibrils both *in vivo* and *in vitro*.[73] The large enhancement of its fluorescence emission upon attachment to fibrils makes ThT a particularly powerful and convenient tool.

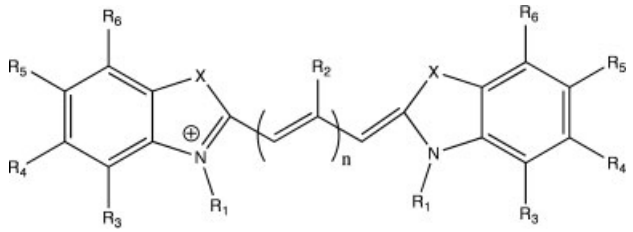


Figure 6. General structure of the polymethine dye (cyanine).

Similarly, examples of chiral complexes between helical peptides and Congo red[74] were reported. In both cases, the structure of the peptide acted as chiral methyl orange template for the aggregation of the dye, inducing selectively the formation of J or H dye aggregates,[75] or temperature-dependent chiral aggregation patterns.[76] Special attention was recently paid to biopolymer-induced polymethine dye (cyanine) (Fig. 6) aggregates.[77]

Indeed, cyanines present interesting and rare photophysical and photochemical features, determined by the presence of flexible polymethine segments introduced as side-chains. Vibrations, torsions and rotations around carbon–carbon single bonds lead to efficient, non-radiative dissipation of excitation energy. Upon restriction of intramolecular mobility, the non-radiative processes are delayed, with enhancement of the competing processes, the first of which is fluorescence emission. This creates the basis for using cyanines as spectral and fluorescent probes in various molecularly organized media, in particular in systems containing biomacromolecules. Furthermore, cyanines possess the unique property, depending on the conditions and the structure, of forming ordered aggregates of different types, dimers and H- and J-aggregates, which can also be used in the development of probes for biomacromolecules.[78] 3,30-disulfopropyl-5,50-dichlorothiacyanine (Tc) and 3,30-disulfobutyl-5,50-diphenyl-9-ethyloxacarbocyanine (Oc) form J-aggregates in aqueous solution in the presence of NaCl, $Mg(NO_3)_2$, D-/L-tartaric acids, asparagine, proline, DNA and proteins such as lysozyme, trypsin, RNase and gelatin. In the presence of chiral additives, optically active J-aggregates are formed, characterized by sigmoidal kinetics with half-times of 10–1000 s, resonance fluorescence and large CD amplitudes of up to 2° for Tc. Generally, the induced CD signals of the J-aggregates of both dyes are bisignate and the sign corresponds to that of the additive. The transfer of chirality information occurs in the course of the J-aggregation. These features make the described Tc and Oc J-aggregates powerful sensors of point chirality and conformational chirality.[79]

In other hybrid cases, the chromophore, which is spatially located in but not covalently bound to the protein (ground state), actually binds to a specific residue of the protein upon the occurrence of an external stimulus, e.g. light. A representative example is the light–oxygen–voltage domain, a common domain of many photosensor proteins in higher plants.[80]

In conclusion, in spite of the interesting examples provided by Nature, attempts to prepare photoresponsive smart materials from proteins with dispersed dyes appear still limited.

Polysaccharide blends

Several polysaccharides, such as chitin, chitosan, galactomannans, cellulose and starch, are well known to adsorb dye molecules by a combination of electrostatic attraction, van der Waals forces, hydrogen bonding and hydrophobic interactions.[81,82] This ability is of considerable significance to various traditional application fields such as fibre dying and decolourization of the resulting effluent. The specific affinity between dyes and polysaccharides was also used for analytical purposes allowing the quantitative determination of the polymers also at low concentration.[83,84]

The specificity and the stability of the interaction between dyes and polysaccharides were often so high[85,86] that typical behaviour of covalently bonded dyes was observed (see above). This happened particularly in the presence of ionic interactions, as for chitosan, which is made mainly of cationic β-(1,4)-D-glucosamine units, and the anionic dye (4-[4-nitrophenyl) azo]phenyl)aminomethane sulfonate. In this case, dichroic absorption in the UV-visible spectral region was observed as the achiral dye assumed a chiral spatial distribution imposed by the chiral polysaccharide.[87]

When the polysaccharide–dye interaction is not very strong switchable optical properties are observed, as in the case of mixing hyaluronan, an anionic polysaccharide, and a cationic cyanine chromophore in water/methanol solvents.[88] The mixture changes its optical properties from that of the cyanine monomer to that of chiral J-aggregates of the dye. The dye–polysaccharide interaction is promoted by increasing the cyanine/hyaluronan molar ratio, by decreasing the temperature in the range 50 to 30 °C or by decreasing the solvent polarity. Moreover, switching from *R*-chiral to *S*-chiral J-aggregates is induced in the same way in the 30 to 0 °C temperature range due to the conformation transition of the polysaccharide from double helix to random coil.

Polysaccharides with a strong tendency towards a helical conformation, such as amylose and β-1,3-glucans, gave also very stable host–guest complexes by trapping molecules inside their helix.[86,89,90] Self-pooling was observed in a solid film of amylose with 4-[4-(dimethylamino)styryl]-1-docosylpyridinium bromide, a hemicyanine dye.[90] The film showed thermochromic behaviour as it changed colour, darkening with increasing temperature: λ_{max} of the UV-visible absorption band shifted gradually towards the red on increasing the temperature in the range 50–100 °C. Fluorescence emission intensity decreased similarly in the same temperature range.[91]

Electron donor (D)–acceptor (A) oligomers (A–D and A–D–A), where D was oligo(phenylene vinylene) and A was *N*,*N*′-dialkyl-4,4′-bipyridinium and *N*,*N*-dimethylaminostyryl-4-pyridinium moieties, were successfully trapped inside an amylose helix. Encapsulation resulted in increasing fluorescence quantum yield (>10-fold) and photoinduced electron/energy transfer efficient over a distance of 10 Å . This behavior arises from the suppression of the molecular self-quenching by aggregation and/or conformational flexibility.[92]

Carboxymethyl amylose (CMA) exists as a coil of short helical segments in acid solution, while these reminiscent helical segments break down on ionization of the carboxyl groups in neutral and basic solutions.[93] This behaviour was modified in the presence of a cationic cyanine dye that induced the formation of a super-helix mediated by J-aggregation of the dye itself (Fig. 7).[94]

The amount of cyanine forming J-aggregates and giving CMA super-helix was modulated by changing the CMA concentration, pH and degree of substitution. The CD and the fluorescence intensity of the solution were modulated in the same way. The CMA helical conformation could be stabilized in two different ways: by complexation with a cationic dye at acid pH[94] or by host–guest complexation with a hydrophobic dye under neutral or basic conditions.[95] The combination of these two stabilization methods resulted in an extremely stable super-helix hierarchical structure as reported for subsequent complexation of CMA with

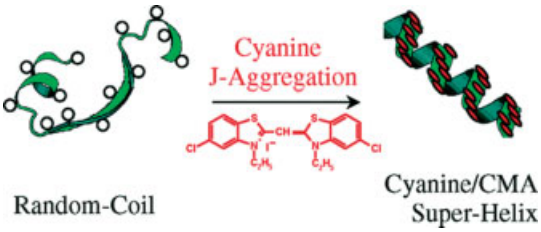


Figure 7. Schematic of CMA super-helix formation mediated by J-aggregation and complexation with a cyanine dye. (Reproduced with permission from Kim *et al.*[94])

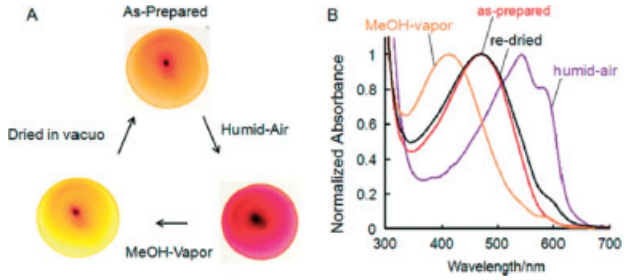


Figure 8. (A) Photographs and (B) normalized UV-visible absorption spectra of a polythiophene–functionalized curdlan film. The as-prepared film was subjected to humid air and methanol vapour and then dried *in vacuo* again. (Reproduced with permission from Shiraki *et al.*[101])

cyanine and D–A cationic oligomers. The cationic nature of the D–A structures prevented their inclusions in CMA with high degree of substitution, except after previous neutralization of the negative charge by complexation with a cationic cyanine dye with cationic D–A species, which could further form a super-helix hierarchical structure.[96]

The inclusion of only an A unit, which was composed of a *N*-dimethylaminostyryl-4-pyridinium moiety with a long alkyl chains, inside the super-helix gave a sharp fluorescence quenching (*ca* 90%) of the cyanine dye J-aggregates at 475 nm. A concomitant enhancement (>20) of the fluorescence from A (at 605 nm) due to energy transfer from the cyanine aggregates.

Other polysaccharides that are well known to assume a helix conformation are (1→3)-β-D-glucans, which can form inclusion complexes with guest molecules and polymers.[97] The wrapping by β-1,3-glucans enforces the entrapped guest polymer to adopt helical or twisted conformations through the convergent interpolymer interactions as for poly(3-[(*R* or *S*)-5-amino-5-carboxyl-3-oxapentyl]-2,5-thiophene hydrochloride) (PT) trapped into schizophyllan (SPG). This last is (1→3)-β-D-glucan with one (1→6)-β-D-glucose side-chain linked at every third main-chain glucose.[18,19] The individual polysaccharide in water exists as a right-handed triple helix (t-SPG) whereas the individual PT derivatives assume a left- or right-handed *syn* type helical arrangement, depending on the substituent configuration. However, right-handed co-helical complexes were formed by both PT derivatives when trapped into the polysaccharide helix.[98]

Similar to amylose, chemical modification of (1→3)-β-D-glucan resulted in less stable helix structures, in particular single-stranded right-handed structures formed instead of triple-stranded ones.[99] This resulted in increased polysaccharide dynamics in solution that allowed the formation of host–guest inclusion complexes by simply mixing in water with poly(cytidylic acid), permethyldecasilane or single-walled carbon nanotubes.[99,100] An inclusion complex was also obtained upon simply mixing in water a cationic polythiophene with curdlan (Fig. 8).[101]

No similar solvent vapour chromism was observed for films obtained with large curdlan excess with respect to the dye or with schizophyllan due to the higher stability of the two systems with respect to complex disaggregation, thus indicating the metastability of the complex as a requisite to responsive materials.

Bio-related polyester blends

The optical response of dye-doped thermoplastic polymer matrices was analysed in depth as a tool to control and to modulate the degree of dispersion of chromophores in the amorphous phase of polymers.[102–104] Various parameters were taken into account: (1) nature of the dye; (2) nature of the continuous polymer matrix; and (3) type of dispersion route. The basic principle of these chromogenic polymer composites is founded on colour changes in absorption or in emission associated with structural modifications of the molecular assemblies of dyes dispersed in the continuous polymeric amorphous phase. Depending on both the processing conditions and dye–polymer interphase interactions, molecularly dispersed dye molecules can aggregate in either the ground or excited state to yield stacked structures characterized by different optical properties.[103–105] In this context, different organic chromophores were incorporated into thermoplastic polymers at various concentrations (from 0.05 to 1 wt%) by processing in the melt. Interestingly, the controlled modulation of the degree of dispersion of the chromophore allowed to obtain binary polymeric mixtures suitable for the preparation of smart flexible or rigid polymeric optical indicators of external stimuli (temperature,[106–111] mechanical stress and pressure[112–120]) and of innovative renewable luminescent materials for energy technology.[121]

The results previously obtained for polyolefin-based materials were effectively applied to biodegradable plastics and bio-based polymer products such as PLA and PBS. Aliphatic polyesters are the most convenient for packaging applications, owing to availability from renewable resources, easy optimization of thermomechanical properties and expected decreasing production costs. The effects of the dispersion of dyes into PLA and PBS were recently analysed.[121–127] More specifically, bis(benzoxazolyl)stilbene (BBS; Fig. 9) attracted particular interest since it belongs to a well-known class of stilbene derivatives generally employed as optical brighteners in many polymer articles and textiles.

PBS films with various concentrations of BBS were prepared in solution or by processing in the melt; after leaving the films to return slowly at room temperature, the characteristic emission depended on the BBS concentration.[123–125] Green luminescence attributed to chromophoric aggregates (*mechanochromic effects*) was observed with 0.1 wt% or more of BBS. The polymer reorganization induced by uniaxial stretching at room temperature disrupted the BBS supramolecular assemblies leading to a prevalent blue emission typical of isolated chromophore molecules. The excimer band at 500 nm of BBS–PBS films containing 0.1 wt% of dye significantly decreased in intensity I_E at 40–50% film elongation (i.e. from $I_E/I_M = 0.8$ at 0% to $I_E/I_M = 0.4$ at 40%), and was completely suppressed at higher elongation (Fig. 9).

Significant interest has been shown in the development of thermochromic polymer blends of a supporting thermoplastic polymer matrix containing small amounts (0.01–3 wt%) of dispersed chromogenic sensor dyes.[107–110,128–130] Kinetically trapped molecular dyes inside the glassy amorphous phase of host

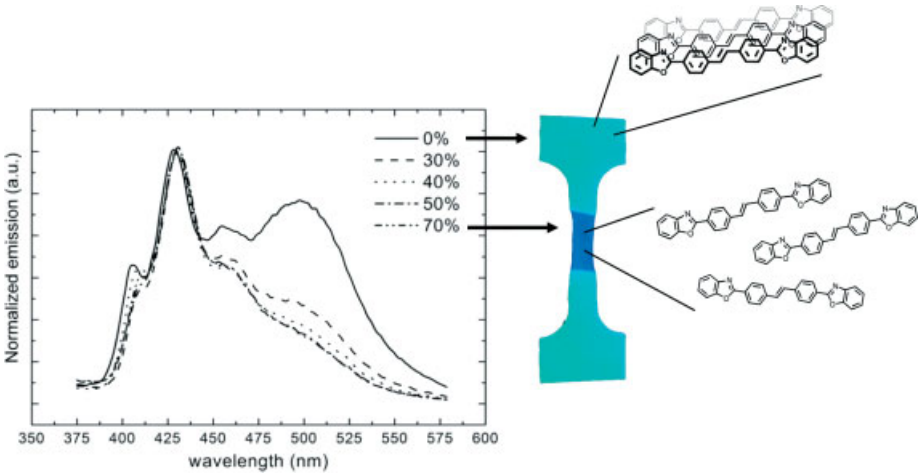


Figure 9. Fluorescence emission spectra of 0.1 wt% PBS–BBS film, before (0%) and after solid-state drawing (from 30 to 70% elongation). The spectra are normalized to the intensity of the isolated BBS molecule peak (430 nm). Digital image of the same film, recorded under excitation at 366 nm (50% elongation). (Adapted with permission from Pucci *et al.*[123])

polymers can be thermally driven to aggregate, thus returning to the thermodynamically favoured stacked structure above a certain threshold temperature; the consequent emission variation produces the sensing mechanism (*thermochromic effects*). Along these lines, thermochromic polymer blends were also realized starting from the aggregachromic dye BBS dispersed (0.02–0.2 wt%) in semicrystalline biodegradable PBS by processing in the melt. The BBS–PBS mixtures after rapid quenching from the melt at 0 °C gave the typical emission of isolated BBS molecules kinetically trapped within the polymer matrix without formation of excimers. Phase separation due to BBS segregation into aggregates occurred on increasing the temperature (50 to 80 °C) as indicated by the colour change of the material from blue (emission at about 440 nm) to green (emission at about 500 nm).[123]

PLA has a slightly lower refractive index (*ca* 1.45) than PMMA (1.49), as well as the same good processability. The reduction of the maximum trapped light due to the lower refractive index is negligible, i.e. 74 and 72% for PMMA and PLA matrices, respectively. For this reason PLA is a viable alternative to PMMA as a transparent and eco-sustainable matrix of luminescent solar concentrators. Low-molecular-weight PLA-based films (number-average molecular weight of about 15 000–20 000 g mol^{-1}) either chemically modified or blended with an oligothiophene luminescent dye (3′-(2-hydroxyethyl)quinquethiophene) appeared very stable under white light irradiation, and exhibited a fluorescence quantum yield that is significantly higher (*ca* 35%) when compared to samples with PMMA as transparent matrix. Moreover, microscopy imaging analysis of the same films indicated a uniform dye distribution within the polymer sample with homogeneous fluorescence intensity of the emission profile both in the *xy*-plane and along the *z*-direction, which confirmed also the absence of preferential segregation of the dye thus excluding luminescence quenching phenomena. Therefore, PLA could have the potential of being even superior to PMMA in terms of optical requirements, but certainly has the great advantage of being a renewable polymer matrix. As far as the thermomechanical properties of PLA are concerned, a suitable amount of a polymer having the required features, such as PBS, can be blended in order to modulate the final properties of the material. It was found that the addition of 15 wt% PBS resulted in significantly improved PLA ductility, as resulting from lower Young's modulus and higher strain at break. Moreover, it is worth noting that the blend exhibited a thermodynamic immiscibility between the amorphous phases of the two polymers (two glass transition temperatures were detected), even if a good blend compatibility was observed using electron microscopy. Moreover, the crystalline PLA content is higher in the blend compared with pure PLA film, likely attributed to the role of PBS nanodroplets as crystallization nuclei for PLA. These characteristics mean that the polyester blend is a valuable matrix for the preparation of polymeric threshold temperature indicators. As a matter of fact, the temperature responsiveness of a PLA-based material was achieved by blending with a minor amount (15 wt%) of PBS. In detail, blends containing 0.07 wt% of BBS dye and consisting of 85 wt% of PLA and 15 wt% of PBS showed an evident change of their luminescent properties from blue to green when thermally driven at temperatures (>60 °C) higher than the glass transition temperature of PLA suggesting that BBS passed from a molecularly dissolved state to a supramolecular architecture.[126] This phenomenon occurring on varying the temperature can possibly be attributed to effects provided by the temperature on the thermally induced mobility and change of polymer matrix thermal features. The passage of the matrix from the glassy to the viscous state promoted by thermal driving induces the cold crystallization of PBS, the crystals of which act as crystallization nuclei for PLA, thus strongly favouring the aggregation of BBS chromophores dispersed in the amorphous phases of the blend (Fig. 10).

Therefore, the presence of 15 wt% of PBS, in which the dye is less soluble than in PLA, is the key factor in promoting BBS aggregation. Thus, upon passage of the matrix from the glassy to the viscous state, BBS is prompted to aggregate to an extent that is temperature-dependent, providing a clear change of the optical characteristics of the blend film.

SYSTEMS COMPARISON AND FINAL REMARKS

Even if the examples described in this mini-review are limited in number when compared to the known synthetic and natural systems based on bio-related polymers and containing organic chromophores, we believe they are sufficient to demonstrate the enormous potential of these systems as well as their usefulness in the preparation of bio-related polymer-based devices

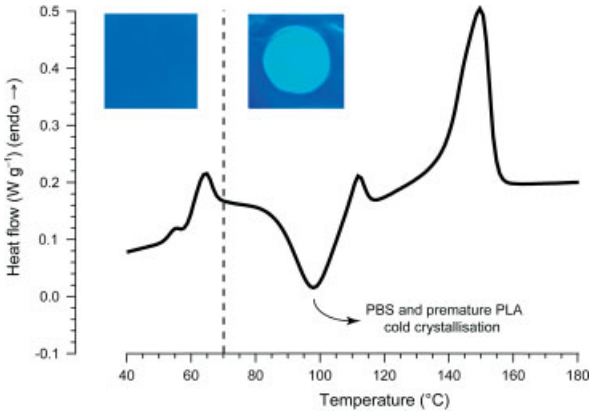


Figure 10. First heating differential scanning calorimetry scan of a blend composed of 85 wt% of PLA and 15 wt% of PBS and containing 0.07 wt% of BBS dye and images of the same film taken under irradiation at 366 nm before (left) and after (right) thermal annealing at 70 °C. (Adapted with permission from Pucci *et al*.[126])

combining an environmentally friendly character with modulated photoresponse.

Two general concepts which go beyond the trivial expected effects concerning colour change and traceability produced by a dye when bound to or dispersed in a material were evidenced and adequately supported with a number of clear examples. These concepts derive from the possibility of using, on the one hand, a radiation absorbing unit, an organic dye, as a trigger for photoinduced response of the involved macromolecules and, on the other hand, as an optical sensor of stimuli affecting the whole material. The structures demonstrating the former concept are those were the macromolecule–chromophore binding is strong and short, as often happens with covalent direct bonding. The trigger efficiency is dependent on the intensity of the changes induced by the radiation and by the trigger concentration and can be enhanced by changes of polarity produced by the photochemical event and synergic action by the environment.

The second general concept was instead developed by dispersing a dye in a polymer and realizing conditions under which self-organization, in particular aggregation–disaggregation, can be determined by submitting the whole material to mechanical and thermal effects, the optical changes observed allowing one to register and evaluate the impact.

The results obtained to date for preparing optically responsive polymers by combining a thermoplastic polymer with a dye either by covalent binding or molecular/aggregate dispersion provide basic information to identify routes for designing these important materials targeted at a large number of advanced applications. Among these, the most promising is certainly the preparation of *luminescent solar concentrators*, thin, flat plates of highly fluorescent material that absorb sunlight and concentrate most of the resulting fluorescence to the edges through total internal reflection.[131–137]

ACKNOWLEDGEMENT

This work was partially supported by the Fondazione CARIPI-Pisa in the frame of the POLOPTEL Research Project.

REFERENCES

1 Pieroni O and Ciardelli F, *Trends Polym Sci* **3**:282–387 (1995).
2 Berkovic G, Krongauz V and Weiss V, *Chem Rev* **100**:1741–1754 (2000)
3 Ciardelli F, Bronco S, Pieroni O and Pucci A, Photoswitchable polypeptides, in *Molecular Switches*, ed. by Feringa BL and Browne WR. Wiley-VCH, Weinheim, pp. 321–360 (2011).
4 Sisido M, *Prog Polym Sci* **17**:699–764 (1992).
5 Cooper TM, Natarajan LV and Crane RL, *Trends Polym Sci* **1**:400–405 (1993).
6 Irie M, Adv Polym Sci **94**:27–67 (1990).
7 Pieroni O, Fissi A and Popova G, *Prog Polym Sci* **23**:81–123 (1998).
8 Ciardelli F, Pieroni O, Fissi A, Altomare A , Solaro R and Tirelli N, *Polym Adv Technol* **6**:32–41 (1995).
9 Ciardelli F, Pieroni O, Fissi A and Houben JL, *Biopolymers* **23**:1423–1437 (1984).
10 Irie M, Miyatake O, Uchida K and Eriguchi T, *J Am Chem Soc* **116**:9894–9900 (1994).
11 Giancotti V, Quadrifoglio F and Crescenzi V, *J Am Chem Soc* **94**:297–298 (1972).
12 Erenrich EH, Andreatta RH and Scheraga HA, *J Am Chem Soc* **92**:1116–1119 (1970).
13 Ueno A, Anzai J, Osa T and Kadoma Y, *J Polym Sci Polym Lett* **15**:407–410 (1977).
14 Ueno A, Anzai J and Osa T, *J Polym Sci Polym Lett* **17**:149–154 (1979).
15 Ulysse L, Cubillos J and Chmielewski J, *J Am Chem Soc* **117**:8466–8467 (1995).
16 Fissi A, Pieroni O, Ruggeri G and Ciardelli F, *Macromolecules* **28**:302–309 (1995).
17 Ciardelli F, Fabbri D, Pieroni O and Fissi A, *J Am Chem Soc* **111**:3470–3472 (1989).
18 Fissi A, Pieroni O, Ciardelli F, Fabbri D, Ruggeri G and Umezawa K, *Biopolymers* **33**:1505–1517 (1993).
19 Yu B, Jiang X, Wang R and Yin J, *Macromolecules* **43**:10457–10465 (2010).
20 Lee H, Wu W, Oh J, Mueller L, Sherwood G, Peteanu L *et al*, *Angew Chem Int Ed* **46**:2453–2457 (2007).
21 Jin Q, Liu G and Ji J, *J Polym Sci A: Polym Chem* **48**:2855–2861 (2010).
22 Kotharangannagari VK, Sanchez-Ferrer A, Ruokolaine J and Mezzenga R, *Macromolecules* **44**:4569–4573 (2011).
23 Cooper TM, Obermeier KA, Natarajan LV and Crane RL, *Photochem Photobiol* **55**:1–7 (1992).
24 Pieroni O, Fissi A, Viegi A, Fabbri D and Ciardelli F, *J Am Chem Soc* **114**:2734–2736 (1992).
25 Alonso M, Reboto V, Guiscardo L, San Martın A and Rodrıguez-Cabello JC. *Macromolecules* **33**:9480–9482 (2000).
26 Margulies D, Melman G and Shanzer A, *J Am Chem Soc* **128**:4865–4871 (2006).
27 Tomizaki K and Mihara H, *J Am Chem Soc* **129**:8345–8352 (2007).
28 Gilmanshin R, Williams S, Callender RH, Woodruff WH and Dyer RB, *Proc Natl Acad Sci USA* **94**:3709–3713 (1997).
29 Munoz V, Thompson PA, Hofrichter J and Eaton J, *Nature* **390**:196–199 (1997).
30 Duan KA and Kollmann PA, *Science* **282**:740–744 (1998).
31 Bieri O, Wirz J, Hellrung B, Schutkowski M, Drewello M and Kiefhaber T, *Proc Natl Acad Sci USA* **96**:9597–9601 (1999).
32 Pieroni O, Fissi, Angelici Nand Lenci F, *Acc Chem Res* **34**:9–17 (2001).
33 Bredenbeck J, Helbing J, Sieg A, Schrader T, Zinth W, Renner C *et al*, *Proc Natl Acad Sci USA* **100**:6452–6457 (2003).
34 Wondraczek H, Kotiaho A, Fardim P and Heinze T, *Carbohydr Polym* **83**:1048–1061 (2011).
35 Bragd PL, van Bekkum H and Besemer AC, *Topics Catal* **27**:49–66 (2004).
36 Heinze TT, Liebert T and Koschella A, *Esterification of Polysaccharides*. Springer-Verlag, Berlin (2006).
37 Heinze T and Liebert T, *Prog Polym Sci* **26**:1689–1762 (2001).
38 Kurita K, *Prog Polym Sci* **26**:1921–1971 (2001).
39 Singha V, Kumara P and Sangh R, *Prog Polym Sci* **37**:340–364 (2012).
40 Graeme M, *Prog Polym Sci* **36**:218–237 (2011).
41 Koschella A, Fenn D, Illy N and Heinze T, *Macromol Symp* **244**:59–73 (2006).
42 Elchinger PH, Faugeras PA, Boëns B, Brouillette F, Montplaisir D, Zerrouki R *et al*, *Polymer* **3**:1607–1651 (2011).
43 Karakawa M, Chikamatsu M, Vakamoto C, Maeda Y, Kubota S and Yase K, *Macromol Chem Phys* **208**:2000–2006 (2007).
44 Karakawa M, Chikamatsu M, Yoshida Y, Azumi R, Yase K and Nakamoto C, *Macromol Rapid Commun* **28**:1479–1484 (2007).

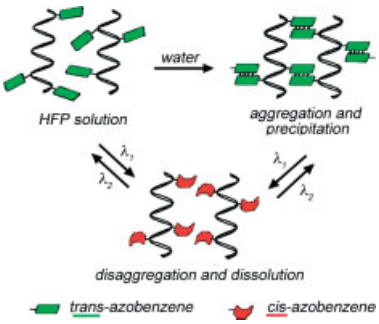
45 Gomez JAC, Erler UW and Klemm DO, *Macromol Chem Phys* **197**:953–964 (1996).
46 Redl FX, Lutz M and Daub J, *Chem Eur J* **7**:5350–5358 (2001).
47 Sakakibara K and Nakatsubo F, *Cellulose* **15**:825–835 (2008).
48 Sakakibara K, Ogawa Y and Nakatsubo F, *Macromol Rapid Commun* **28**:1270–1275 (2007).
49 Edahiro JI, Sumaru K, Takagi T, Shinbo T and Kanamori T, *Langmuir* **22**:5224–5226 (2006).
50 Arai K and Kawabata Y, *Macromol Rapid Commun* **16**:875–880 (1995).
51 Urban MW (ed.), *Handbook of Stimuli-Responsive Materials*. Wiley-VCH, Weinheim (2011).
52 Feringa BL, van Delden RA, Koumura N and Geertsema EM, *Chem Rev* **100**:1789–1816 (2000).
53 Arai K, Shitara Y and Ohyama T, *J Mater Chem* **6**:11–14 (1996).
54 Lee MH, Li XD and Kim E, *Mol Cryst Liq Cryst* **349**:51–54 (2000).
55 Bertoldo M, Nazzi S, Zampano G and Ciardelli F, *Carbohydr Polym* **85**:401–407 (2011).
56 Suizhou Y, Monsy MJ, Li L, Cholli AL, Kumar J and Tripathy SK, *Macromolecules* **34**:9193–9196 (2001).
57 Klok HA, Becker S, Schuch F, Pakula T and Mullen K, *Macromol Biosci* **3**:729–741 (2003).
58 Ciardelli G, Saad B, Lendlein A, Neuenschwander P and Suter UW, *Macromol Chem Phys* **198**:1481–1498 (1997).
59 Nakagawa K, Aono T, Ueda G, Tsutsumi C, Hayase N, Mabuchi M *et al*, *Sens Actuators B* **108**:542–546 (2005).
60 Katz JS, Zhong S, Ricart BG, Pochan DJ, Hammer DA and Burdick JA, *J Am Chem Soc* **132**:3654–3655 (2010).
61 Shi D, Matsusaki M and Akashi M, *J Control Release* **149**:182–189 (2011).
62 Thi TH, Matsusaki M and Akashi M, *Biomacromolecules* **10**:766–772 (2009).
63 Du J, Fang YY and Zheng YB, *Polymer* **48**:5541–5547 (2007).
64 Zhang GQ, Fiore GL, Clair TLS and Fraser CL, *Macromolecules* **42**:3162–3169 (2009).
65 Fattori V, Melucci M, Ferrante L, Zambianchi M, Manet I, Oberhauser W *et al*, *Energy Environ Sci* **4**:2849–2853 (2011).
66 Slomkowski S, Gadzinowski M, Sosnowski S, Radomska-Galant I, Pucci A, De Vita C *et al*, *J Nanosci Nanotechnol* **6**:3242–3251 (2006).
67 Chen M and Besenbacher F, *ACS Nano* **5**:1549–1555 (2011).
68 Burns DC, Flint DG, Kumita JR, Feldman HJ, Serrano L, Zhang Z *et al*, *Biochemistry* **43**:15329–15338 (2004).
69 Nakasone Y, Zikihara K, Tokutomi S and Terazima M, *Biophys J* **99**:3831–3839 (2010).
70 Lougheed T, Borisenko V, Hennig T, Ruck-Braun K and Woolley GA, *Org Biomol Chem* **2**:2798–2801 (2004).
71 Schutt M, Krupka SS, Milbradt AG, Deindl S, Sinner EK, Oesterhelt D *et al*, *Chem Biol* **10**:487–490 (2003).
72 Burns DC, Zhang F and Woolley GA, *Nature Protocols* **2**:251–258 (2007).
73 Kuo CH, Fruk L and Niemeyer CM, *Chem Asian J* **4**:1064–1069 (2009).
74 Biancalana M and Koide S, *Biochim Biophys Acta* **1804**:1405–1412 (2010).
75 Cooper TM and Stone MO, *Langmuir* **14**:6662–6668 (1998).
76 Takahashi D, Tanabe R and Izumi T, *J Polym Sci A: Polym Chem* **49**:1691–1698 (2011).
77 Tatikolov AS, *J Photochem Photobiol C* **13**:55–90 (2012).
78 Yang QF, Xiang JF, Li Q, Yan WP, Zhou QJ, Tang YL *et al*, *J Phys Chem B* **112**:8783–8787 (2008).
79 Slavnova TD, Gorner H and Chibisov AK, *J Phys Chem B* **115**:3379–3384 (2011).
80 Demarsy E and Fankhauser C, *Curr Opin Plant Biol* **12**:69–74 (2009).
81 Blackburn RS, *Environ Sci Technol* **38**:4905–4909 (2004).
82 Yamaki SB, Barros DS, Garcia CM, Socoloski P, Oliveira Jr ON and Atvars TDZ, *Langmuir* **21**:5414–5420 (2005).
83 Edstrom RD, *Anal Biochem* **29**:421–432 (1969).
84 Soedjak HS, *Anal Chem* **66**:4514–4518 (1994).
85 Wood PJ and Fulcher RG, *Cereal Chem* **55**:952–966 (1978).
86 Numata M, Tamesue S, Fujisawa T, Haraguchi S, Hasegawa T, Bae A-H *et al*, *Org Lett* **8**:5533–5536 (2006).
87 Kumar S and Koh J, *J Appl Polym Sci* **124**:4897–4903 (2012).
88 Sagawa T, Tobatab H and Ihara H, *Chem Commun* 2090–2091 (2004).
89 Malik S, Fujita N, Numata M, Ogura K and Shinkai S, *J Mater Chem* **20**:9022–9024 (2010).
90 Kim O-K, Choi L-S, Zhang H-Y, He X-H and Shih Y-H, *J Am Chem Soc* **118**:12220–12221 (1996).
91 Choi LS and Kim O-K, *Macromolecules* **31**:9406–9408 (1998).
92 Kim O-K, Je J and Melinger JS, *J Am Chem Soc* **128**:4532–4533 (2006).
93 Rao VSR and Foster JF, *Biopolymers* **3**:185–193 (1965).
94 Kim O-K, Je J, Jernigan G, Buckley L and Whitten D, *J Am Chem Soc* **128**:510–516 (2006).
95 Sanji T, Kato N and Tanaka M, *Macromolecules* **39**:7508–7512 (2006).
96 Kim O-K, Melinger J, Chung S-J and Pepitone M, *Org Lett* **10**:1625–1628 (2008).
97 Numata M and Shinkai S, *Chem Commun* **47**:1961–1975 (2011).
98 Haraguchi S, Tsuchiya Y, Shiraki T, Sugikawa K, Sada K and Shinkai S, *Chem Eur J* **15**:11221–11228 (2009).
99 Ikeda M, Hasegawa T, Numata M, Sugikawa K, Sakurai K, Fujiki M *et al*, *J Am Chem Soc* **129**:3979–3988 (2007).
100 Lien LTN, Shiraki T, Dawn A, Tsuchiya Y, Tokunaga D, Tamaru S-i *et al*, *Org Biomol Chem* **9**:4266–4275 (2011).
101 Shiraki T, Dawn A, Tsuchiya Y and Shinkai S, *J Am Chem Soc* **132**:13928–13935 (2010).
102 Pucci A, Ruggeri G, Bronco S, Signori F, Donati F, Bernabo M *et al*, *Prog Org Coat* **72**:21–25 (2011).
103 Pucci A and Ruggeri G, *J Mater Chem* **21**:8282–8291 (2011).
104 Pucci A, Bizzarri R and Ruggeri G, *Soft Matter* **7**:3689–3700 (2011).
105 Pucci A, Tirelli N, Ruggeri G and Ciardelli F, *Macromol Chem Phys* **206**:102–111 (2005).
106 Crenshaw BR and Weder C, *Adv Mater* **17**:1471–1476 (2005).
107 Kinami M, Crenshaw BR and Weder C, *Chem Mater* **18**:946–955 (2006).
108 Crenshaw BR, Kunzelman J, Sing CE, Ander C and Weder C, *Macromol Chem Phys* **208**:572–580 (2007).
109 Donati F, Pucci A, Boggioni L, Tritto I and Ruggeri G, *Macromol Chem Phys* **210**:728–735 (2009).
110 Donati F, Pucci A and Ruggeri G, *Phys Chem Chem Phys* **11**:6276–6282 (2009).
111 Weder C, *Chimia* **63**:758–763 (2009).
112 Donati F, Pucci A, Cappelli C, Mennucci Band G. Ruggeri, *J Phys Chem B* **112**:3668–3679 (2008).
113 Pucci A, Bertoldo M and Bronco S, *Macromol Rapid Commun* **26**:1043–1048 (2005).
114 Pucci A, Biver T, Ruggeri G, Itzel Meza Land Pang Y. *Polymer* **46**:11198–11205 (2005).
115 Crenshaw BR, Burnworth M, Khariwala D, Hiltner A, Mather PT, Simha R *et al*, *Macromolecules* **40**:2400–2408 (2007).
116 Caruso MM, Davis DA, Shen Q, Odom SA, Sottos NR, White SR *et al*, *Chem Rev* **109**:5755–5798 (2009).
117 Davis DA, Hamilton A, Yang J, Cremar LD, Van Gough D, Potisek SL *et al*, *Nature* **459**:68–72 (2009).
118 Kunzelman J, Gupta M, Crenshaw BR, Schiraldi DA and Weder C, *Macromol Mater Eng* **294**:244–249 (2009).
119 Pucci A, Donati F, Ruggeri G and F. Ciardelli, *e-Polymers* **058** (2009).
120 Sagara Y and Kato T, *Nature Chem* **1**:605–610 (2009).
121 Fattori V, Melucci M, Ferrante L, Zambianchi M, Manet I, Oberhauser W *et al*, *Energy Environ Sci* **4**:2849–2853 (2011).
122 Burkinshaw SM and Jeong DS, *Dyes Pigm* **92**:1025–1030 (2012).
123 Pucci A, Di Cuia F, Signori F and Ruggeri G, *J Mater Chem* **17**:783–790 (2007).
124 Fourati MA, Maris T, Bazuin CGand Prud'homme RE, *Acta Crystallogr C* **66**:o11–o14 (2010).
125 Fourati MA, Maris T, Skene WG, Bazuin CG and Prud'homme RE, *J Phys Chem B* **115**:12362–12369 (2011).
126 Pucci A, Signori F, Bizzarri R, Bronco S, Ruggeri G and Ciardelli F, *J Mater Chem* **20**:5843–5852 (2010).
127 Blackburn RS, Zhao XF, Farrington DW and Johnson L, *Dyes Pigm* **70**:251–258 (2006).
128 Dei S, Matsumoto A and Matsumoto A, *Macromolecules* **41**:2467–2473 (2008).
129 Koopmans C and Ritter H, *J Am Chem Soc* **129**:3502–3503 (2007).
130 Uchiyama S, Matsumura Y, Prasanna de Silva A and Iwai K, *Anal Chem* **75**:5926–5935 (2003).
131 Reisfeld R, *Opt Mater* **32**:850–856 (2010).
132 van Sark WGJHM, Barnham KWJ, Slooff LH, Chatten AJ, Buchtemann A, Meyer A *et al*, *Opt Express* **16**:21773–21792 (2008).
133 Chatten AJ, Barnham KWJ, Buxton BF, Ekins-Daukes NJ and Malik MA, *Semiconductors* **38**:909–917 (2004).
134 El Shahawy MA and Mansour AF, *J Mater Sci Mater Electr* **7**:171–174 (1996).
135 Neuroth N and Haspel R, *Solar Energy Mater* **16**:235–242 (1987).
136 Zewail AH and Batchelder JS, *ACS Symp Ser* **220**:331–352 (1983).
137 Hermann AM, *Solar Energy* **29**:323–329 (1982).

Published online in Wiley Online Library:

(wileyonlinelibrary.com) DOI 10.1002/pi.4395

Mini-review

The structure and optical response of eco-compatible smart materials are described, with bio-related polypeptides, polysaccharides and polyesters as the macromolecular partner in combination with selected bound or blended organic chromophores.



The unique optical behaviour of bio-related materials with organic chromophores **000**

Francesco Ciardelli,* Monica Bertoldo, Simona Bronco, Andrea Pucci, Giacomo Ruggeri and Francesca Signori

