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Supramolecular ordered photochromic cholesteric polymers as smart labels for thermal monitoring applications

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ABSTRACT

New reversible temperature-sensitive polymeric materials with a broad window of trigger temperatures were developed for application as thermal monitoring smart labels for perishable commodities. In particular new liquid crystalline copolymers functionalized with azoaromatic chromophores and chiral cholesteric moieties were synthesized by Controlled Radical Polymerization (CRP) using cheap and easily available reagents and mild reaction conditions. These materials exhibit a chiral nematic phase (N*) with an intense Bragg reflection which gives an iridescent and bright appearance to their thick films. By inducing the azoaromatic *trans-cis* isomerization through UV irradiation, it is possible to break the native chiral supramolecular conformational order thus leading to an amorphous transparent phase which is characterized by different UV–Vis and CD spectra and which is stable whilst the temperature is kept below the T_g of the polymer. Hence, tags can be reused even though the required process is so specific that they cannot be easily tampered. Thus, owing to the high control of the polymer molecular weight and structure allowed by the ATRP technique, it is possible to finely tune the trigger temperature and the photoswitchable properties thus allowing the fabrication of tailor made labels suitable for a huge variety of products with potential applications as sensors and in photonic and display fields.

1. Introduction

The ability to guarantee the full traceability of a product, with a particular focus on the validation of the conservation conditions along the production and transportation chain, represents a notable issue for contemporary agroindustrial and pharmaceutical markets. Since such a certification represents an added value for temperature-sensitive products, many devices have indeed been developed for thermal monitoring applications. As an example, Scriba Nanotechnology developed multi-functional labels able to provide the items they are applied to with authentication, cold-chain reliability validation and traceability features [1–3]. These tags, based on hologram pictures, can act as thermal monitoring devices for the pharmaceutical cold chain thanks to the integration of a polymer layer that changes the aspect of the hologram when a specified temperature threshold is breached, as well as to store digital data in the hologram substrate; however, at the present time the wide applicability of such tags is hampered by the cost of the production technology. Other more common and simple commercial labels are Time-Temperature Indicators (TTIs) [4–10] which provide visual signals of the temperature history of a product during the distribution and storage stage. In most cases these systems are based on thermally sensitive dyes [11,12] which undergo an irreversible chemical transformation above a certain temperature and their applicability is restricted to a small range of trigger temperatures hence limiting their use on a large scale. Additionally the induction of a supramolecular helical order in polymers has been the subject of intense research, not only for the hypothesis of its occurrence at the early stages of life on earth [13] but also for its potential applications in material science, such as in chiroptical switching, reversible optical storage [14–16], chiral amplification [17,18], chiral discrimination and chiroptical sensors [19]. To induce chirality in soft matter, two different structural

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levels must be mainly considered: the molecular and the supramolecular ones. The former is provided by the chirality of molecules, which is of configurational and conformational origin; the latter arises from the organization of molecules with formation of a chiral superstructure by means of long-range positional and orientational orders of molecules [20].

In this context, optically active and temperature-sensitive cholesteric polymers are of great interest for the fabrication of such devices. It was previously reported, indeed, that Liquid Crystal (LC) photochromic polymers functionalized with azoaromatic mesogens and chiral moieties, can attain supramolecular ordered helix conformations that result in intensely coloured cholesteric phases [21,22]. Such a behaviour is due to the formation of supramolecular helical structures which lead to visible light diffraction phenomena (Bragg reflection).

Indeed, it is well-known that a cholesteric mesophase is characterized by the helical supramolecular organization of mesogens which determines its unique optical properties [23], such as the selective reflection of light with wavelength (λ_{max}) depending on the helix pitch (P) of the cholesteric structure, according to the equation

$$\lambda_{max} = P\bar{n}$$

where $\bar{n}$ is the average refractive index of liquid crystal.

Owing to the presence of the azoaromatic groups which can provide *trans-cis* photoisomerization upon irradiation with light of a suitable wavelength, it is possible to destroy this supramolecular order thus obtaining an amorphous isotropic transparent material [21,22]. Since this process is reversible, by appropriately tuning the phase transition temperatures of the polymer, it could be possible to develop new devices able to memorize the thermal history of the item they are applied onto and with tailored switching temperatures.

Indeed, the isotropic uncoloured phase is stable until the temperature is kept below the polymer glass transition temperature (T_g); above it, the macromolecules will rearrange and the cholesteric phase with its bright colour will be restored. In this way the material could record its thermal history by evidencing it through macroscopic changes, becoming very interesting for the production of smart labels.

It is worth noting that the thermal properties of the material are very important because T_g usually represents the trigger temperature at which the macroscopic change happens. Thus, with the aim to obtain materials with precisely tailored thermal properties, the synthesis of macromolecules with defined structure and average molecular weight appears to be a key issue in the governing of the thermal transitions location [24]. In particular the present work reports the synthesis of (meth)acrylic homo- and random copolymers bearing in the side chain photochromic azoaromatic groups and/or chiral cholesteric moieties (Scheme 1). The synthesis was carried out by Atom Transfer Radical Polymerization (ATRP) [25,26] in order to obtain well defined macromolecules characterized by low polydispersity and different molecular weights: the application of a controlled radical polymerization leading to tailored (co)-polymers allowed the study of the correlations between structure and thermal properties together with their tendency to form liquid crystalline cholesteric phases. Furthermore, a particular attention was given to the use of cheap and easily available reagents and mild reaction conditions, with the aim to obtain new functional materials with reasonable costs, thus suitable for industrial applications.

For the sake of comparison polydispersed homo- and copolymer analogues were synthesized by classic free radical polymerization (FRP) in presence of AIBN as thermal initiator, in order to outline the benefits attained by the use of a controlled polymerization technique.

2. Materials and methods

2.1. Materials

The monomers 4-ethoxy-3′-methyl-4′-(6-acryloyloxyhexyloxy) azobenzene (**A6MA**) [27], 6-acryloyloxy-hexanoyl-1-cholesterol (**A6C**) [28] and 6-methacryloyloxy-hexanoyl-1-cholesterol (**M6C**) [28] were synthesized as reported in the literature.

4-Ethoxy-3′-methyl-4′-(6-methacryloyloxyhexyloxy) azobenzene (**M6MA**) was synthesized with a procedure analogues to what reported in the literature for **A6MA** [27].

Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized as previously reported [29].

2,2′-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use.

Tetrahydrofuran (THF) and anisole were purified and dried according to the reported procedures [30] and stored under nitrogen.

Allyl 2-bromoisobutyrate (ABIB), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), copper bromide and all the other reagents and solvents were purchased from Aldrich and used as received.

2.1.1. Synthesis of acrylic polymers

All the polymerizations were carried out in glass vials using allyl 2-bromo-2-methylpropionate (ABIB) as initiator, tris[2-(dimethylamino)ethyl]amine (Me_6TREN) as ligand, Cu(I)Br as catalyst and dry anisole as solvent (monomer concentration 0.24 M). Several reaction mixtures {[monomer]/[ABIB]/[Me_6TREN]/[CuBr]=50:1:1:1 by mol} were introduced into the vials under nitrogen atmosphere, submitted to several freeze–thaw cycles and heated at 80 °C for 7 days. The obtained polymers were purified by chromatography (eluent CH_2Cl_2/CH_3OH 9:1 v:v) then precipitated in cold hexane or methanol. The products were finally dried at 70 °C under vacuum for several days up to constant weight.

Relevant data for the synthesized polymers are reported in Table 1. All the products were characterized by FT-IR, ^1H and ^{13}C NMR. As an example, the spectroscopic data for Poly(**A6MA**), Poly(**A6C**) and Poly(**A6MA**-*co*-**A6C**)-(83:17) are reported hereafter.

*2.1.1.1. Poly(**A6MA**).* FT-IR (ATR): 3069 (ν_{CH} Ar), 2935 e 2860 (ν_{CH} aliph.), 1727 ($\nu_{C=O}$ ester), 1598 and 1580 ($\nu_{C=C}$ Ar), 1392 (δ_{CH} CH_3), 1142 and 1106 (ν_{CO} ether), 840 and 829 (δ_{CH} Ar 1,4 disubst.), 730 (δ_{CH} Ar 1,3,4 trisubst.) cm^{-1}.

^1H NMR ($CDCl_3$): 7.95–7.75 (2H, Ar 2-H), 7.75–7.56 (2H, Ar 2′-H and 6′-H), 7.06–6.85 (2H, Ar 3-H), 6.85–6.68 (1H, Ar 5′-H), 5.39–5.12 (2H, ABIB CH_2=CH–), 4.52 (2H, ABIB CH_2–O), 4.22–3.76 (6H, CH_2–O; main chain CH), 2.34–2.13 (3H, CH_3–Ar), 1.93–1.01 (8H, alkyl spacer CH_2; 3H, CH_3–CH_2–O; main chain CH_2) ppm.

^{13}C NMR ($CDCl_3$): 175.2 (C=O), 161.2 and 159.7 (Ar 4-C and 4′-C), 147.4 and 146.8 (Ar 1-C and 1′-C), 127.8 (Ar 3′-C(CH_3)), 124.6 and 123.8 (Ar 2-C, 2′-C and 6′-C), 115.0 (Ar 5′-C), 110.9 (Ar 3-C), 68.4 (ABIB CH_2–O), 64.1 (CH_3–CH_2–O), 63.2 (COOCH_2–), 42.3 (main chain CH_2–CH), 29.6, 26.3, 26.1, 25.9 (alkyl spacer CH_2 and main chain CH_2–CH), 16.7 (CH_3–Ar), 15.1 (CH_3–CH_2–O) ppm.

*2.1.1.2. Poly(**A6C**).* FT-IR (KBr): 2938 and 2867 (ν_{CH} aliph.), 1733 ($\nu_{C=O}$ ester), 1384 (δ_{CH} CH_3), 1167 (ν_{CO} ester) cm^{-1}.

^1H NMR ($CDCl_3$): 5.38 (2H, **A6C** CH_2=CH–), 4.68–4.49 (1H, CH–O; 2H, ABIB CH_2–O), 4.16–3.88 (3H, CH_2–O and main chain CH), 2.38–2.20 (4H, CH_2–COO and **A6C** CH_2–CH=), 2.14–0.56 (−49H, **A6C** and alkyl spacer CH, CH_2 and CH_3, and main chain CH_2–CH) ppm.