Reactive & Functional Polymers 72 (2012) 469–477

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Synthesis and photoresponsive behavior of optically active methacrylic homopolymers containing side-chain spiropyran chromophores

Luigi Angiolini [a], Tiziana Benelli [a,*], Erika Bicciocchi [b], Loris Giorgini [a], Françisco M. Raymo [c]

[a] Dip. di Chimica Industriale e dei Materiali and INSTM UdR-Bologna, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy
[b] CSIRO Molecular and Health Technologies, Bag 10, Clayton South, Victoria 3169, Australia
[c] Laboratory for Molecular Photonics, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, FL 33146-0431, USA

ARTICLE INFO

Article history:
Received 27 October 2011
Received in revised form 13 March 2012
Accepted 23 April 2012
Available online 27 April 2012

Keywords:
Photochromic chiral polymers
Circular dichroism
Spiropyrans
Photochromism
Polymeric chiroptical switches

ABSTRACT

Novel optically-active methacrylic homopolymers bearing in the side chain one or more chiral groups of one single configuration (based on the L-lactic acid residue) linked to the spiropyran chromophore, have been successfully synthesized and fully characterized.

These intrinsically chiral polymers exhibit remarkable thermal stability, with glass transition temperatures in the range 100–130 °C and decomposition temperatures around 270 °C. The chiroptical characterization indicates the occurrence of asymmetric induction on the electronic transitions of the side-chain chromophore related to the number of L-lactic acid residues interposed between the main chain and the spiropyran chromophore.

In the presence of acid, these systems can be used to modulate the protonation of polymeric azopyridine moieties upon photoisomerization of the spiropyran group. In addition to UV–Vis spectroscopy, the proton transfer process occurring between the macromolecular components can be also followed by CD spectroscopy, the system thus behaving as a chiroptical switch.

1. Introduction

An intense interest has currently arisen toward investigations dealing with the amplification of chirality of polymeric materials, in solution as well as in the solid state [1–4]. To this regard, in previous studies we reported on optically active photochromic methacrylic polymers bearing in the side chain both a chiral group of one single configuration (i.e. the L-lactic acid residue) and *trans*-azoaromatic [5,6] or porphyrin chromophores [7] that provide the macromolecules with the further possibility of assuming a conformational dissymmetry of one prevailing screw sense, which can be revealed by the presence, in the circular dichroism (CD) spectra, of dichroic bands related to the electronic transitions of the chromophore [8]. This functional combination allows the polymers to display additional properties typical of dissymmetric systems (optical activity, exciton splitting of chiroptical absorptions) which are of interest in the field of chiral nanotechnology [9,10].

On the other hand, photochromic materials are well known candidates for several technological applications, such as devices for the optical storage of information, optical switches and, in general, as materials exhibiting photoresponsive properties when irradiated with light of suitable frequency and intensity [11–13].

An important class of photochromic compounds includes derivatives of spiropyran (SP) and spirooxazine, which are characterized by a marked photochromism [14–17]. It is well known that the colorless SP, upon irradiation with ultraviolet (UV) light, isomerizes to the purple merocyanine open form (ME) through heterolytic cleavage of the spiro carbon–oxygen bond. The process is thermally and photochemically reversible. Furthermore, the photogenerated open form, after addition of acid, switches completely to the protonated species (MEH) which, if irradiated with visible light, releases a proton and switches back to the SP form. The absorption and emission properties of these three species (SP, ME and MEH) significantly differ and allow to use these compounds for repeated data recording and optical data storage [14,18–23] (Fig. 1).

Fascinating strategies to implement memory devices based on these spiropyran photochromic compounds have indeed been proposed, such as the intermolecular communication between different molecular switches based on photon and/or proton transfer [19,20,24].

Recently [25], we also reported the possibility to couple an homopolymeric methacrylic spirobenzopyran system, poly[1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline)] {poly[**M-SP**]}, with a polymer functionalized with chiral azopyridine moieties, poly[(*S*)-3-methacryloyloxy-1-[4-(2-pyridilazo)phenyl] pyrrolidine] {poly[(*S*)-**AZ**]}, which can exist in the unprotonated {poly[(*S*)-**AZ**]} and protonated form {poly[(*S*)-**AZH**]} (Fig. 2).

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* Corresponding author. Tel./fax: +39 051 2093720.
E-mail address: tiziana.benelli@unibo.it (T. Benelli).

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http://dx.doi.org/10.1016/j.reactfunctpolym.2012.04.011

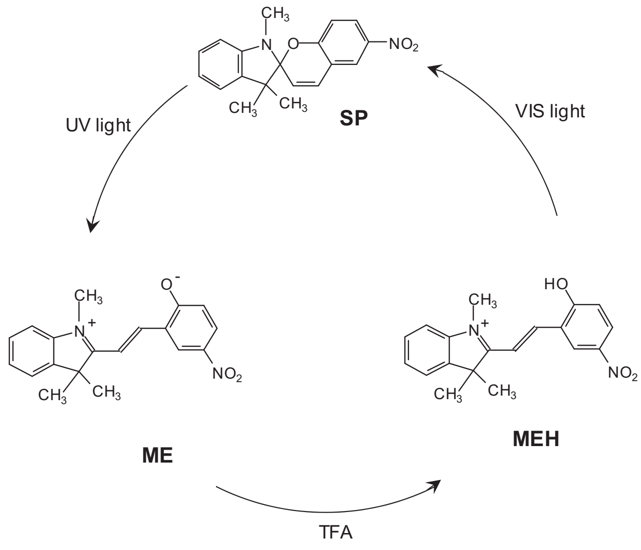


Fig. 1. The switching cycle associated with the three species **SP**, **ME** and **MEH**.

It was observed that the proton release by the protonated azopyridine compound to the ME species can be modulated by controlling the interconversion between SP and ME through UV and Vis light irradiation [20,24,25] and that the obtained signal communication between these polymeric switches can be monitored not only by UV–Vis spectroscopy, but also by CD [25], owing to the presence in poly[(*S*)-**AZ**] of a chiral group of one prevailing configuration (i.e. the pyrrolidine residue) interposed between the polymeric backbone and the *trans*-azopyridine chromophore.

Although numerous investigations have been devoted to photosensitive polymers containing spiropyran side groups [14,17,22,26], to our knowledge, polymeric systems bearing two distinct functional groups (i.e. spiropyran and chiral groups of one single absolute configuration) directly linked to the side chain have not yet been reported and could be of potential interest for several advanced applications and to investigate the influence of the macromolecular chirality on the peculiar properties of this particular group of photoresponsive polymeric derivatives.

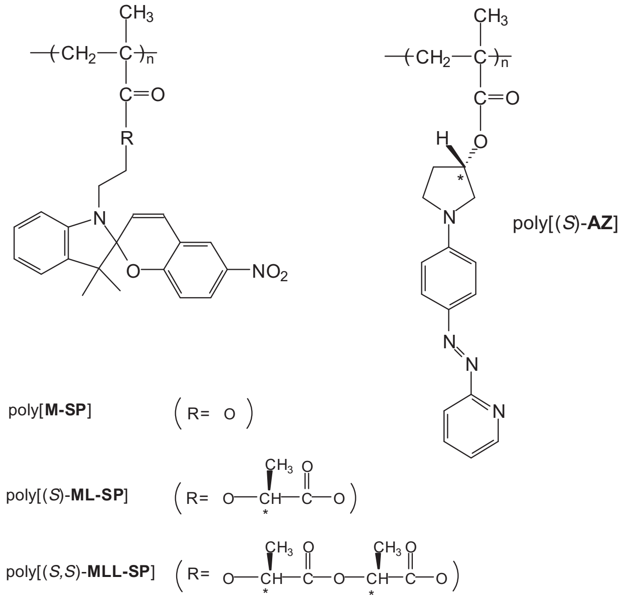


Fig. 2. Chemical structures of the investigated polymers.

In this context, we considered the opportunity of preparing and investigating a new group of optically-active methacrylic polymers bearing in the side chain one or two chiral groups of one single configuration based on the L-lactic acid residue linked to the photochromic spiropyran chromophore, in order to use this material in combination with poly[(*S*)-**AZ**], so as to observe the hydrogen transfer also when these distinct macromolecular systems are both optically active.

To this purpose, in the present article we describe the preparation of the chiral polymeric derivatives poly[1′-{2-[(*S*)-2-methacryloyloxypropanoyloxy]ethyl}-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline)] {poly[(*S*)-**ML-SP**]} and poly[1′-(2-{(*S*)-2-[(*S*)-2-methacryloyloxypropanoyloxy]propanoyloxy}ethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline)] {poly[(*S,S*)-**MLL-SP**]} (Fig. 2). These new polymeric materials have been characterized by common spectroscopic techniques with particular attention to their thermal, chiroptical and photochromic properties.

The photoisomerization with UV and/or Vis light of the spiropyran moiety, in the presence of trifluoroacetic acid (TFA), has been investigated in the presence of poly[(*S*)-**AZ**] and the photoresponsive properties, as well as the resulting signal communication between these macromolecular switches, observed by UV–Vis and CD spectroscopy.

2. Experimental

2.1. Physico-chemical characterization

^{1}H and ^{13}C NMR spectra were obtained at room temperature, on 5–10% w/v $CDCl_3$ solutions, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm from tetramethylsilane (TMS) as the internal reference. ^{1}H NMR spectra were run at 300 MHz by using the following experimental conditions: 24,000 data points, 4.5-kHz spectral width, 2.6-s acquisition time, 128 transients. ^{13}C NMR spectra were recorded at 75.5 MHz under full proton decoupling by using the following experimental conditions: 24,000 data points, 20-kHz spectral width, 0.6-s acquisition time, 64,000 transients. FT-IR spectra were carried out on a Perkin–Elmer 1750 spectrophotometer equipped with an Epson Endeavor II data station, on samples prepared as KBr pellets.

Number average molecular weights of the polymers ($\overline{M}_n$) and their polydispersity index ($\overline{M}_w/\overline{M}_n$) were determined in THF solution by SEC using an HPLC Lab Flow 2000 apparatus equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5-micron MXL column and a UV–Vis detector Linear Instrument model UVIS-200, working at 254 nm. Calibration curves were obtained by using monodisperse polystyrene standards in the range 800–35,000.

The glass transition temperature values (T_g) of polymers were determined by differential scanning calorimetry (DSC) on a TA Instrument DSC 2920 Modulated apparatus adopting a temperature program consisting of three heating and two cooling ramps starting from room temperature (heating/cooling rate 10 °C/min under nitrogen atmosphere) on samples of 5–9 mg.

The initial thermal decomposition temperature (T_d) was determined on the polymeric samples with a Perkin–Elmer TGA-7 thermogravimetric analyzer by heating the samples in air at a rate of 20 °C/min.

Checking of liquid crystalline behavior was carried out with a Zeiss Axioscope2 polarizing microscope through crossed polarizers fitted with a Linkam THMS 600 hot stage.

Optical activity measurements were accomplished at 25 °C on dichloroethane solutions ($c \approx 0.250\ g\ dL^{-1}$) with a Perkin Elmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 1 dm. Specific optical rotation values at the sodium D line are expressed as deg dm^{-1} g^{-1} cm^3.

UV–Vis absorption spectra of the samples in solution were recorded at 25 °C in dichloroethane with a Varian Cary 100 Bio spectrophotometer. The spectral region 800–220 nm was investigated by using cells path length of 0.1 cm at chromophore concentration of about 5.0×10^{-4} mol L^{-1}.

CD spectra were carried out on a Jasco 810 A dichrograph, under the same conditions as the UV–Vis spectra. The $\Delta\varepsilon$ values, expressed as L mol^{-1} cm^{-1}, were calculated from the following expression: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg cm^2 $dmol^{-1}$ refers to one spiropyran chromophore.

Irradiations experiments at 365 nm were carried out at 25 °C on dichloroethane solutions (2 mL) using the same cells path length and solution concentrations as the UV–Vis and CD measurements, with a Mineralight UVGL-25 lamp. Irradiations at 436 nm were carried out in the same conditions using the emission from a 150 W medium pressure Hg lamp (Hanau), filtered by a 436 nm interference filter (Balzer) with a ±5 nm bandwidth.

2.2. Materials

Methacryloyl chloride (Sigma–Aldrich, Milan, Italy) was distilled (bp 95 °C) under inert atmosphere in the presence of traces of 2,6-di-*tert*-butyl-*p*-cresol as polymerization inhibitor just before use. (+)-L-Lactic acid (Aldrich), 1,3-diisopropylcarbodiimide (**DIPC**, Aldrich) and 4-dimethylaminopyridine (Aldrich) were used as received. 4-Dimethylaminopyridinium 4-toluensulfonate (**DPTS**) was prepared from 4-dimethylaminopyridine and 4-toluensulfonic acid as described [27].

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

Methylene dichloride (CH_2Cl_2), dichoroethane (DCE) and tetrahydrofuran (THF) were purified and dried according to reported procedures [28] and stored over molecular sieves (4 Å) under nitrogen.

All other reagents and solvents (Aldrich) were used as received without further purification.

2-(3′,3′-Dimethyl-6-nitro-3′H-spiro[chromene-2,2′-indol]-1′-yl)-ethanol (**SP-OH**) [29], (*S*)-(−)-methacryloyl-L-lactic acid [(*S*)-**ML]** [30] and poly[(*S*)-3-methacryloyloxy-1-[4-(2-pyridylazo)phenyl] pyrrolidine] {poly[(*S*)-**AZ**]} [25] were prepared as reported.

2.3. Synthesis of the spiropyran monomers

The spiropyran alcohol **SP-OH** (13.5 mmol) was added at room temperature under nitrogen flow to a solution of the chiral acid (*S*)-**ML** (13.5 mmol) in dry CH_2Cl_2 (20 mL), in the presence of 2,6-di-*tert*-butyl-p-cresol (0.10 g) as polymerization inhibitor. **DIPC** (2.7 mL, 17.6 mmol), and **DPTS** (13.5 mmol) were added to the stirred solution as coupling agent and as condensation activator, respectively [27]. The mixture was kept at room temperature for 48 h, the solid N,N′-diisopropylurea formed filtered off and the organic solution washed repeatedly with aq. 0.1 M HCl, 5% Na_2CO_3 and H_2O, in that order. After drying the organic layer on anhydrous Na_2SO_4 and evaporation of the solvent under vacuum, the crude mixture of products was purified by column chromatography in the dark (SiO_2, CH_2Cl_2 as eluent) obtaining three products, i.e. **M-SP**, (*S*)-**ML-SP** and (*S,S*)-**MLL-SP**, in the pure form, which were characterized as follows.

2.3.1. 1′-(2-Methacryloyloxyethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline) [*M-SP*]. Yield 40%

^{1}H NMR: 8.06 and 8.02 (d and s, 2H, arom. *ortho* to nitro group), 7.22–6.80 (m, 5H, arom.), 6.70 (d, 1H, C*H*=CH—CO), 6.10 and 5.60 (d, 2H, CH_2=), 5.90 (d, 1H, CH=C*H*—CO), 4.30 (m, 2H, CH_2—O), 3.60–3.35 (m, 2H, CH_2—N), 1.90 (s, 3H, methacrylic CH_3), 1.30 and 1.15 (2s, 6H, indoline CH_3) ppm.

FT-IR: 3081 (ν_{CH} arom.), 2946 (ν_{CH} aliph.), 1713 ($\nu_{C=O}$), 1637 ($\nu_{C=C}$ methacrylic), 1611 and 1509 ($\nu_{C=C}$ arom.), 1162 (ν_{C-O}), 809 and 743 (δ_{CH} arom. rings) cm^{-1}.

2.3.2. 1′-{2-[(S)-2-Methacryloyloxypropanoyloxy]ethyl}-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline) [(S)-*ML-SP*]. Yield 24%

^{1}H NMR: 8.05 and 7.95 (d and s, 2H, arom. *ortho* to nitro group), 7.30–6.70 (m, 5H, arom.), 6.60 (d, 1H, C*H*=CH—CO), 6.20 and 5.65 (d, 2H, CH_2=), 5.90 (d, 1H, CH=C*H*—CO), 5.15 (q, 1H, C*H*—CH_3), 4.30 (m, 2H, CH_2—O), 3.60–3.35 (m, 2H, CH_2—N), 1.95 (s, 3H, methacrylic CH_3), 1.45 (d, 3H, CH_3—CH), 1.30 and 1.15 (2s, 6H, indoline CH_3) ppm.

^{13}C NMR: 170.9 (C=O lactic ester), 167.3 (C=O methacrylic ester), 159.8, 147.8, 143.6, 142.0, 136.2, 129.1, 128.5, 126.4, 123.2, 122.7, 120.6, 119.1, 116.2, 107.3 and 107.1 (*C*H=*C*H pyran), 136.0 (CH_2=*C*—CH_3), 126.2 (CH_2=), 69.5 (CH_3—*C*H), 63.8 (*C*(CH_3)$_2$), 53.3 (CH_2—O), 42.6 (CH_2—N), 26.5 and 20.3 (indoline CH_3), 18.2 (methacrylic CH_3), 17.4 (*C*H_3—CH) ppm.

FT-IR: 3080 (ν_{CH} arom.), 2961 (ν_{CH} aliph.), 1750 ($\nu_{C=O}$ lactic ester), 1723 ($\nu_{C=O}$ methacrylic ester), 1640 ($\nu_{C=C}$ methacrylic), 1611 and 1509 ($\nu_{C=C}$ arom.), 1385 (δ CH_3), 1160 (ν_{C-O}), 807 and 744 (δ_{CH} arom. rings) cm^{-1}.

2.3.3. 1′-(2-{(S)-2-[(S)-2-Methacryloyloxypropanoyloxy]propanoyloxy}ethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline) [(S,S)-*MLL-SP*]. Yield 12%

^{1}H NMR: 8.05 and 7.95 (d and s, 2H, arom. *ortho* to nitro group), 7.30–6.70 (m, 5H, arom.), 6.60 (d, 1H, C*H*=CH—CO), 6.20 and 5.65 (d, 2H, CH_2=), 5.90 (d, 1H, CH=C*H*—CO), 5.20–5.05 (m, 2H, C*H*—CH_3), 4.30 (m, 2H, CH_2—O), 3.60–3.35 (m, 2H, CH_2—N), 1.95 (s, 3H, methacrylic CH_3), 1.45 (d, 3H, C*H*$_3$—CH—COO—CH), 1.30 and 1.15 (2s, 6H, indoline CH_3) ppm.

^{13}C NMR: 170.9, 170.7 (C=O lactic ester), 167.3 (C=O methacrylic ester), 159.9, 147.8, 143.4, 141.8, 136.3, 129.2, 128.4, 126.5, 123.4, 122.5, 120.7, 119.1, 116.2, 107.4 and 107.1 (*C*H=*C*H pyran), 136.1 (CH_2=*C*—CH_3), 126.1 (CH_2=), 69.6 and 69.2 (CH_3—*C*H), 63.9 (*C*(CH_3)$_2$), 53.4 (CH_2—O), 42.8 (CH_2—N), 26.4 and 20.4 (indoline CH_3), 18.3 (methacrylic CH_3), 17.4 (*C*H_3—CH) ppm.

FT-IR: 3076 (ν_{CH} arom.), 2956 (ν_{CH} aliph.), 1748 ($\nu_{C=O}$ lactic ester), 1723 ($\nu_{C=O}$ methacrylic ester), 1639 ($\nu_{C=C}$ methacrylic), 1610 and 1509 ($\nu_{C=C}$ arom.), 1386 (δ CH_3), 1159 (ν_{C-O}), 807 and 744 (δ_{CH} arom. rings) cm^{-1}.

2.4. Synthesis of polymeric derivatives

The homopolymerization reactions of (*S*)-**ML-SP** and (*S,S*)-**MLL-SP** were carried out in glass vials using 2,2′-azobisisobutyronitrile (AIBN) as thermal initiator (2 wt% with respect to the monomers) and dry THF as solvent (0.5 g of monomer in 5 mL of THF). The reaction mixture were introduced into the vial under nitrogen atmosphere, submitted to several freeze–thaw cycles and heated at 60 °C for 72 h. The reactions were then stopped by pouring the mixtures into a large excess (100 mL) of methanol, and the coagulated polymer filtered off. The solid polymeric products were purified by repeated precipitations in methanol and finally dried under vacuum to constant weight.

The dried polymers were soluble in THF and $CHCl_3$ as well as in strong polar solvents such as nitrobenzene, DMF, DMA or DMSO. Relevant data for the synthesized products are reported in Table 1.

Conversions were determined gravimetrically and all the products characterized by FT-IR, ^{1}H and ^{13}C NMR.

2.4.1. Poly[1′-{2-[(S)-2-methacryloyloxypropanoyloxy]ethyl}-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline)] {poly[(S)-**ML-SP**]}

^{1}H NMR: 8.05–7.85 (m, 2H, arom. *ortho* to nitro group), 7.20–6.50 (m, 5H, arom. and 1H, $\mathrm{C}\mathit{H}{=}\mathrm{CH{-}CO}$), 5.95–5.75 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{{-}CO}$), 5.00–4.75 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{{-}CH_3}$), 4.40–4.05 (m, 2H, $\mathrm{CH_2{-}O}$), 3.60–3.20 (m, 2H, $\mathrm{CH_2{-}N}$), 2.10–0.40 (m, 5H, backbone $\mathrm{CH_3}$ and $\mathrm{CH_2}$, 6H, indoline $\mathrm{CH_3}$ and 3H, $\mathrm{C}\mathit{H_3}\mathrm{{-}CH}$) ppm.

^{13}C NMR: 177.4 ($\mathrm{C{=}O}$ methacrylic ester), 170.9 ($\mathrm{C{=}O}$ lactic ester), 159.9, 147.2, 141.8, 136.4, 129.2, 128.5, 126.6, 123.5, 122.5, 120.7, 119.2, 116.2, 107.4 and 107.1 ($\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$ pyran), 69.9 ($\mathrm{CH_3{-}}\mathit{C}\mathrm{H}$), 63.6 ($\mathit{C}\mathrm{(CH_3)_2}$), 55.2 (backbone $\mathrm{CH_2{-}}\mathit{C}$), 53.5 ($\mathrm{CH_2{-}O}$), 45.7 ($\mathit{C}\mathrm{H_2{-}C}$ backbone), 42.9 ($\mathrm{CH_2{-}N}$), 26.5 and 20.5 (indoline $\mathrm{CH_3}$), 19.6 and 17.8 (backbone $\mathrm{CH_3}$), 17.4 ($\mathit{C}\mathrm{H_3{-}CH}$) ppm.

FT-IR: 3042(ν_{CH} arom.), 2952 (ν_{CH} aliph.), 1732 ($\nu_{\mathrm{C=O}}$ lactic and methacrylic ester), 1611 and 1521 ($\nu_{\mathrm{C=C}}$ arom.), 1385 (δ $\mathrm{CH_3}$), 1126 ($\nu_{\mathrm{C-O}}$), 806 and 746 (δ_{CH} arom. rings) $\mathrm{cm^{-1}}$.

2.4.2. Poly[1′-(2-{(S)-2-[(S)-2-methacryloyloxypropanoyloxy]-propanoyloxy}ethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline)] {poly[(S,S)-**MLL-SP**]}

^{1}H NMR: 8.05–7.90 (m, 2H, arom. *ortho* to nitro group), 7.20–6.60 (m, 5H, arom. and 1H, $\mathrm{C}\mathit{H}{=}\mathrm{CH{-}CO}$), 5.95–5.80 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{{-}CO}$), 5.20–4.85 (m, 2H, $\mathrm{C}\mathit{H}\mathrm{{-}CH_3}$), 4.40–4.05 (m, 2H, $\mathrm{CH_2{-}O}$), 3.60–3.30 (m, 2H, $\mathrm{CH_2{-}N}$), 2.10–0.80 (m, 5H, backbone $\mathrm{CH_3}$ and $\mathrm{CH_2}$, 6H, indoline $\mathrm{CH_3}$ and 6H, $\mathrm{C}\mathit{H_3}\mathrm{{-}CH}$) ppm.

^{13}C NMR: 177.5 ($\mathrm{C{=}O}$ methacrylic ester), 170.8 ($\mathrm{C{=}O}$ lactic ester), 160.0, 147.3, 141.8, 136.4, 129.3, 128.5, 126.6, 123.5, 122.5, 120.7, 119.2, 116.2, 107.4 and 107.1 ($\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$ pyran), 69.4 ($\mathrm{CH_3{-}}\mathit{C}\mathrm{H}$), 63.9 ($\mathit{C}\mathrm{(CH_3)_2}$), 55.2 (backbone $\mathrm{CH_2{-}}\mathit{C}$), 53.5 ($\mathrm{CH_2{-}O}$), 45.7 ($\mathit{C}\mathrm{H_2{-}C}$ backbone), 42.9 ($\mathrm{CH_2{-}N}$), 26.5 and 20.5 (indoline $\mathrm{CH_3}$), 19.6 and 17.8 (backbone $\mathrm{CH_3}$), 17.4 ($\mathit{C}\mathrm{H_3{-}CH}$) ppm.

FT-IR: 3042(ν_{CH} arom.), 2969 (ν_{CH} aliph.), 1738 ($\nu_{\mathrm{C=O}}$ lactic and methacrylic ester), 1610 and 1520 ($\nu_{\mathrm{C=C}}$ arom.), 1385 (δ $\mathrm{CH_3}$), 1126 ($\nu_{\mathrm{C-O}}$), 807 and 744 (δ_{CH} arom. rings) $\mathrm{cm^{-1}}$.

3. Results and discussion

3.1. Synthesis and structural characterization

The key intermediate 2-(3′,3′-dimethyl-6-nitro-3′H-spiro[chromene-2,2′-indol]-1′-yl)-ethanol (**SP-OH**) [29] was used to prepare the new optically-active monomers (*S*)-**ML-SP** and (*S,S*)-**MLL-SP** by reaction with the chiral acid (*S*)-**ML** [30] in the presence of **DIPC** and **DPTS** as coupling agent and condensation activator, respectively [27] (Scheme 1).

Under these conditions, **SP-OH** and (*S*)-**ML** may give esterification and transesterification of the methacrylic ester. As a consequence, spirobenzopyran methacrylic monomers with different numbers of lactic acid residues linked together were actually obtained and separated by column chromatography. The structures of the different products achieved along with their relative amounts are reported in Scheme 1.

Taking into account the mild conditions adopted, similar to those reported for the synthesis of other optically active polyesters starting from chiral hydroxy acid reagents reported in the literature [31,32], it is reasonable to presume that no racemization at the asymmetric center occurs during the reaction and therefore that the obtained products are as optically pure as the L-lactic acid precursor.

The structures of the above mentioned products were confirmed by ^{1}H NMR analysis, which displays, besides the resonances of the vinylic protons of monomeric methacrylate (around 5.70 and 6.20 ppm) and the protons of the spiropyran moiety, an increasing number of quartets (substantially overlapped) and doublets due to the lactic acid CH and $\mathrm{CH_3}$ groups, respectively.

Differently from (*S*)-**ML-SP** and (*S,S*)-**MLL-SP**, the achiral monomer **M-SP**, previously synthesized by a different way and already investigated in its homopolymeric form [25], was not submitted to polymerization.

The chiral monomers were then radically homopolymerized in THF solution by adopting the usual method employing AIBN (2% w/w of monomer) as thermal initiator. The obtained polymeric products, purified by repeated dissolution and reprecipitation in methanol, displayed comparable average molecular weight and polydispersity values (Table 1), as determined by SEC, and the expected IR spectra, showing the disappearance of the absorption band at 1636 $\mathrm{cm^{-1}}$, related to the methacrylic double bond. Accordingly, in the ^{1}H NMR spectra, the resonances of the vinylidenic protons of the monomer were absent. The purified polymeric products were completely soluble in several solvents such as $\mathrm{CHCl_3}$, THF, N-methylpyrrolidone, dimethylacetamide, dimethylsulfoxide, this behavior favoring the possibility of their application also as thin films.

The thermal stability of the polymeric derivatives, as determined by thermogravimetric analysis (TGA), resulted good under the adopted conditions, with decomposition temperature values around 271–273 °C (Table 1). Such a behavior is similar to that reported for the analog poly[**M-SP**] [25], lacking of the L-lactic acid residue, and is indicative of a remarkable presence of strong dipolar interactions in the solid state between the chromophores located in the macromolecular side chains, thus making these materials, also, interesting for potential applications.

The observation with a polarizing microscope did not reveal any liquid–crystalline behavior and DSC thermograms showed only second-order transitions, originated by glass transitions (T_g), with no melting peaks, thus suggesting that these materials are substantially amorphous in the solid state (Table 1 and Fig. 3).

As previously reported, poly[**M-SP**] is characterized by a high T_g value (166 °C) which was ascribed to the stiffness and steric hindrance of the spiropyran group located in the side chain [25]. The insertion of an increasing number of lactic acid residues between the backbone and the chromophore, makes the side chain of poly[(*S*)-**ML-SP**] and poly[(*S,S*)-**MLL-SP**] increasingly flexible, however does not prevent the presence in the solid state of strong dipolar interactions between the spiropyran moieties, as demonstrated by their still high T_g values (123 and 99 °C, respectively) (Fig. 3).

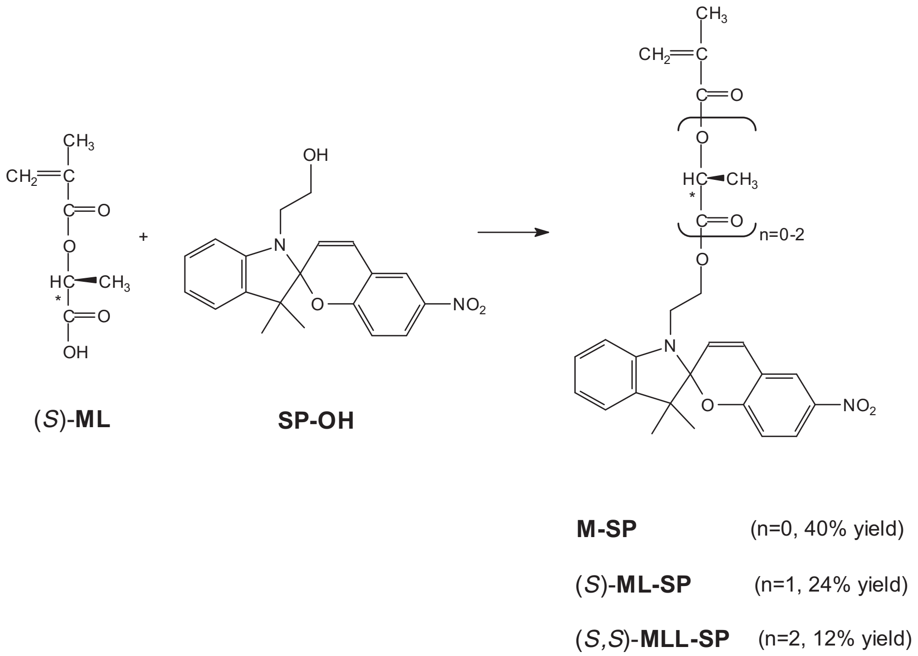
Table 1
Characterization data of polymeric derivatives.

Sample	Yield %	$\overline{M}_{n,SEC}$ [a] g/mol	$\overline{M}_w/\overline{M}_n$ [a]	T_g [b] (°C)	T_d [c] (°C)
Poly[**M-SP**][d]	73	11,800	1.8	166	275
Poly[(*S*)-**ML-SP**]	47	5500	1.8	123	273
Poly[(*S,S*)-**MLL-SP**]	39	5300	1.5	99	271

[a] Determined by SEC in THF at 25 °C.
[b] Determined by DSC, heating rate of 10 °C/min under nitrogen atmosphere.
[c] Determined by TGA, heating rate of 20 °C/min in air.
[d] Ref. [25].

3.2. UV–Vis and photochromic properties

As previously reported for other spiropyran derivatives [20,24,25,33–35], the absorption spectra (Table 2) of colorless solutions of poly[(S)-ML-SP], poly[(*S,S*)-MLL-SP] and of the corresponding monomers show three typical absorption bands: the first one located at 340 nm is related to the internal charge-transfer transition of the spiropyran system; the other two, at 270 and 243 nm, more intense, to the electronic transitions of the individual aromatic rings.



Scheme 1. Synthetic route to the spiropyran monomers.

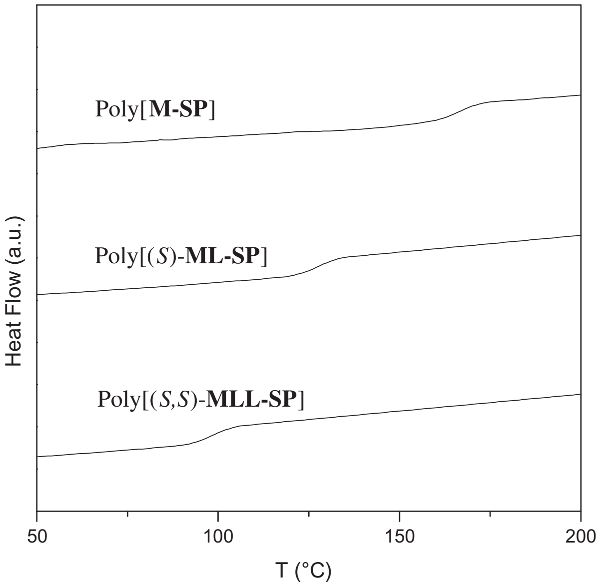


Fig. 3. DSC traces (second heating cycle) of poly[**M-SP**], poly[(*S*)-**ML-SP**] and poly[(*S*,*S*)-**MLL-SP**] at heating rate of 10 °C/min under nitrogen atmosphere.

As an example, the UV–Vis absorption spectra of poly[(*S*)-**ML-SP**] in dichloroethane before and after irradiation at 365 nm and subsequent treatment with one equivalent of TFA are reported in Fig. 4.

By irradiating the solution poly[(*S*)-**ML-SP**] with UV light, the neutral compound switches to the purple zwitterionic merocyanine isomer (ME) because of the cleavage of a C—O bond. Thus, the conjugation between the aromatic rings increases, and an absorption band at 575 nm, related to the merocyanine π–π^* electronic transition, appears. Poly[(*S*,*S*)-**MLL-SP**] and poly[**M-SP**] show similar behavior, except for the intensity of the merocyanine band.

Table 2
UV–Vis spectral data of polymeric compounds and their corresponding monomers in dichloroethane solution at 25 °C.

Samples	1st Band		2nd Band		3rd Band	
	λ_{max}[a]	ε_{max}[b]	λ_{max}[a]	ε_{max}[b]	λ_{max}[a]	ε_{max}[b]
M-SP[c]	341	8700	268	16,400	243	20,200
Poly[**M-SP**][c]	341	8100	269	16,200	243	20,100
(*S*)-**ML-SP**	342	8600	268	16,300	243	20,200
Poly[(*S*)-**ML-SP**]	340	8700	270	16,100	243	20,700
(*S*,*S*)-**MLL-SP**	341	8700	268	16,300	244	20,100
Poly[(*S*,*S*)-**MLL-SP**]	340	8600	269	15,900	243	20,700

[a] Wavelength of maximum absorbance, expressed in nm.
[b] Expressed in L mol^{-1} cm^{-1} and calculated for one single chromophore.
[c] Ref. [25].

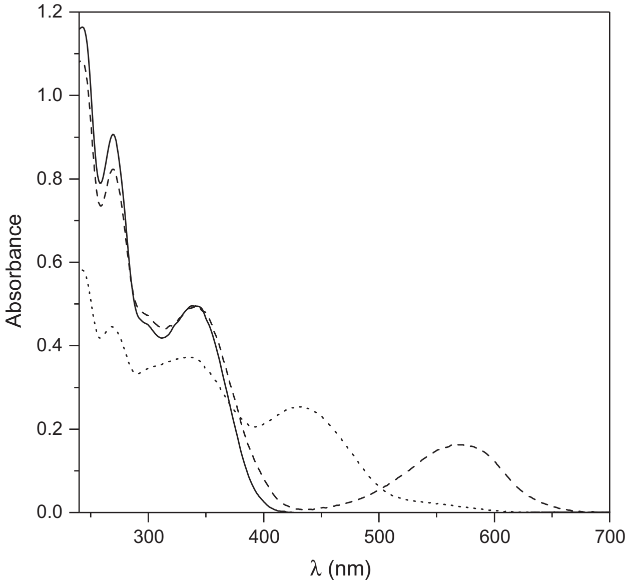


Fig. 4. UV–Vis spectra of poly[(*S*,*S*)-**MLL-SP**] in dichloroethane before (—) and after (- - -) irradiation at 365 nm and subsequent treatment with one equivalent of TFA (···).

By using the molar extinction coefficient of the open form of the parent compound 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′(2*H*)-indole] [36], it is possible to evaluate the amount of ME% at the photostationary state. The obtained data show that, after the same irradiation time, poly[(*S*,*S*)-**MLL-SP**] and poly[(*S*)-**ML-SP**] display lower amounts of open form than the related achiral homopolymer poly[**M-SP**] (21%, 27% and 30%, respectively). By contrast, monomers (*S*)-**ML-SP** and (*S*,*S*)-**MLL-SP**, which do not posses any structural restriction and are randomly dispersed in dilute solution, show amounts of merocyanine form around 9%, similarly to **M-SP** [25,35].

Such a behavior can be ascribed to the occurrence of dipolar interactions between spiropyran chromophores in the side chains, stabilizing the merocyanine form at the equilibrium, which progressively fade when the flexibility of the side chains increases due to the presence of a longer chiral spacer located between the chromophore and the macromolecular backbone.

This hypothesis is confirmed by the different spiropyran back-isomerization rates of solutions stored in the dark. Under these conditions, the merocyanine residue thermally isomerizes back to the initial neutral closed spiropyran form, which is thermodynamically more stable, and the process can be followed by monitoring the absorbance change at 570 nm (Fig. 5). The back-isomerization rates appear almost similar for poly[**M-SP**] [25,35] and poly[(*S*)-**ML-SP**], but relatively faster for poly[(*S*,*S*)-**MLL-SP**] as a direct consequence of the above mentioned reduction of dipolar interchromophoric interactions stabilizing the ME form.

Upon addition of 1 equivalent of TFA to the solution at the photostationary state after UV irradiation, the purple ME form switches to the yellow-green protonated form MEH. Accordingly, the absorption at 575 nm fades and a new band appears at 435 nm (Fig. 4). By irradiating with Vis light, or by adding a base (triethylamine), MEH can be converted again to the initial neutral spiropyran form, thus restoring the original absorption spectrum.

In conclusion, the new chiral polymeric compounds, as well as the corresponding monomers, can switch between three different states, each of them characterized by its own absorption properties. These features, together with their significant thermal stability, suggest the possibility of use for repeated recording of data and optical data-storage applications, similarly to the achiral polymeric derivative poly[**M-SP**].

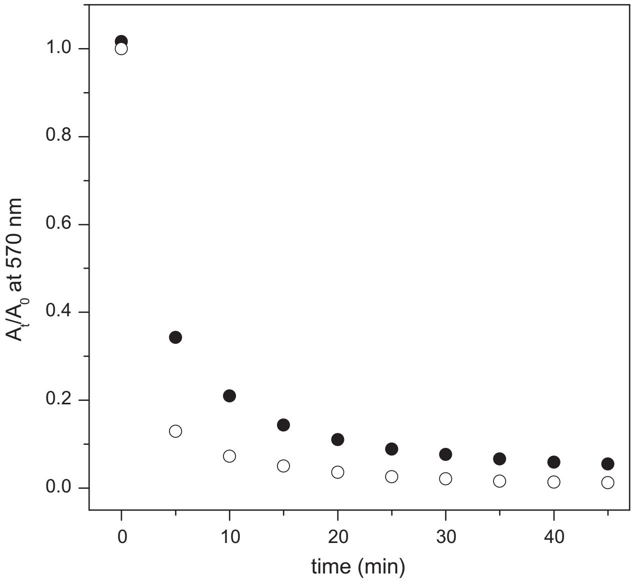


Fig. 5. UV–Vis absorbance values expressed as A_t/A_0 (at 570 nm) of poly[(*S*)-**ML-SP**] (●) and poly[(*S*,*S*)-**MLL-SP**] (○) at 25 °C in dichloroethane solution during thermal back isomerization after irradiation at 365 nm.

3.3. Chiroptical properties of spiropyran derivatives

To investigate the optical activity in dilute solution, the specific and molar optical rotation values at the sodium D line $\{[\alpha]_D^{25}$ and $[\Phi]_D^{25}\}$ (Table 3) were determined for the polymeric derivatives and the CD spectra (Table 4) of all the chiral samples were recorded.

The specific optical rotation values shown by poly[(*S*)-**ML-SP**] and poly[(*S*,*S*)-**MLL-SP**] (−22 and −41 deg dm^{-1} g^{-1} cm^3, respectively) (Table 3) are higher than those of the corresponding monomers (*S*)-**ML-SP** and (*S*,*S*)-**MLL-SP** (−4 and −31 deg dm^{-1} g^{-1} cm^3, respectively) and can be ascribed to the establishment of increased overall dissymmetry in the macromolecules. The remarkable optical activity enhancement shown by the (*S*,*S*)-**MLL** derivatives with respect to the (*S*)-**ML** ones, could be attributed to the increasing number of chiral centers of a single absolute configuration present in each monomeric unit.

As reported in Table 4, the CD spectra of monomeric and polymeric chiral spiropyran derivatives show, in correspondence of the UV–Vis absorption bands (Table 2), dichroic signals of low intensity. The intensities of these bands are significantly higher in the polymer with respect to the corresponding monomer and increase with the number of chiral centers present in the side chain: indeed, the CD spectrum of poly[(*S*,*S*)-**MLL-SP**] is enhanced in amplitude if compared to that one of poly[(*S*)-**ML-SP**] (Table 4 and Fig. 6), in agreement with the observed optical rotation values. A similar trend, although of lower magnitude, is shown by the related monomers (*S*)-**ML-TPP** and (*S*,*S*)-**MLL-TPP**.

The dichroic signals are clearly due to the intrinsic chirality of the L-lactic acid residue, which is able to induce an asymmetric perturbation on the electronic transitions of the spiropyran chromophore giving rise to differential circularly polarized light absorption in solution. As frequently observed in the literature [1–4,8], the optical activity of polymeric derivatives is remarkably higher with respect to the related monomers, in consequence of the restricted conformational mobility due to the macromolecular structure.

Differently from our previous studies [5–7] concerning optically active polymeric derivatives bearing side-chain azoaromatic or porphyrin chromophores, in the present case the spiropyran chromophore does not appear to originate in their CD spectra dichroic excitonic couplets which are usually correlated to the presence of conformational dissymmetry of the macromolecules with a prevailing helix sense. In this case the absence of particularly structured dichroic signals (excitonic couplets) in the CD spectra of the homopolymers suggests that no conformational dissymmetry is present or that the chirally perturbed electronic transitions of the spiropyran chromophores are insufficient to disclose it.

However, the presence in these materials of the spiropyran chromophore possessing induced optical activity, may allow to

Table 3
Specific and molar optical rotation of spiropyran derivatives.

Sample	$[\alpha]_D^{25}$ [a]	$[\Phi]_D^{25}$ [b]
ML-SP	−4	−19.7
Poly[(*S*)-**ML-SP**]	−22	−108.4
MLL-SP	−31	−175.1
Poly[(*S*,*S*)-**MLL-SP**]	−41	−231.5

[a] Specific optical rotation, expressed as deg dm^{-1} g^{-1} cm^3, in dichloroethane solution.

[b] Molar optical rotation, expressed as deg dm^{-1} mol^{-1} dL and calculated as ($[\alpha]_D^{25} \cdot M/100$), where *M* represents the molecular weight of the monomeric unit.

Table 4
CD spectral data of chiral spiropyran derivatives in dichloroethane solution at 25 °C.

Sample	1st Band		2nd Band		3rd Band	
	λ_1[a]	$\Delta\varepsilon_1$[b]	λ_2[a]	$\Delta\varepsilon_2$[b]	λ_3[a]	$\Delta\varepsilon_3$[b]
(*S*)-**ML-SP**	–	–	265	−0.32	246	−0.60
Poly[(*S*)-**ML-SP**]	342	+0.07	268	−0.45	247	−0.66
(*S*,*S*)-**MLL-SP**	–	–	266	−0.41	244	−0.74
Poly[(*S*,*S*)-**MLL-SP**]	343	+0.12	266	−0.60	246	−1.07

[a] Wavelength (in nm) of maximum dichroic absorption.
[b] $\Delta\varepsilon$ expressed in L mol^{-1} cm^{-1} and calculated for one repeating unit in the polymers.

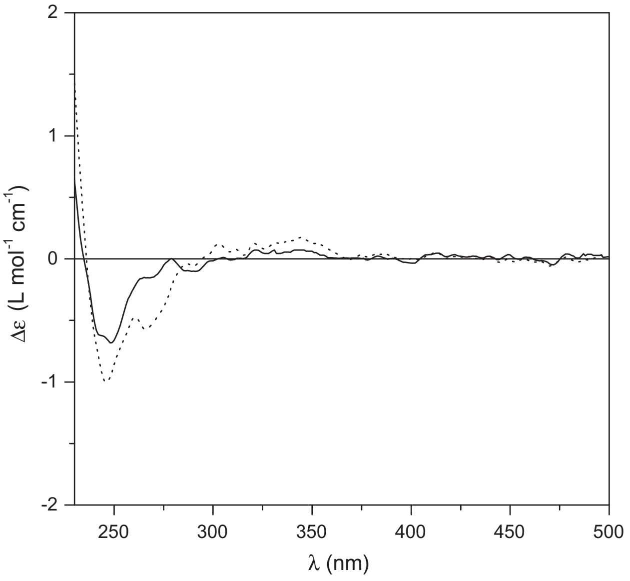


Fig. 6. CD spectra in dichloroethane solution of poly[(*S*)-**ML-SP**] (—) and poly[(*S*,*S*)-**MLL-SP**] (- - -).

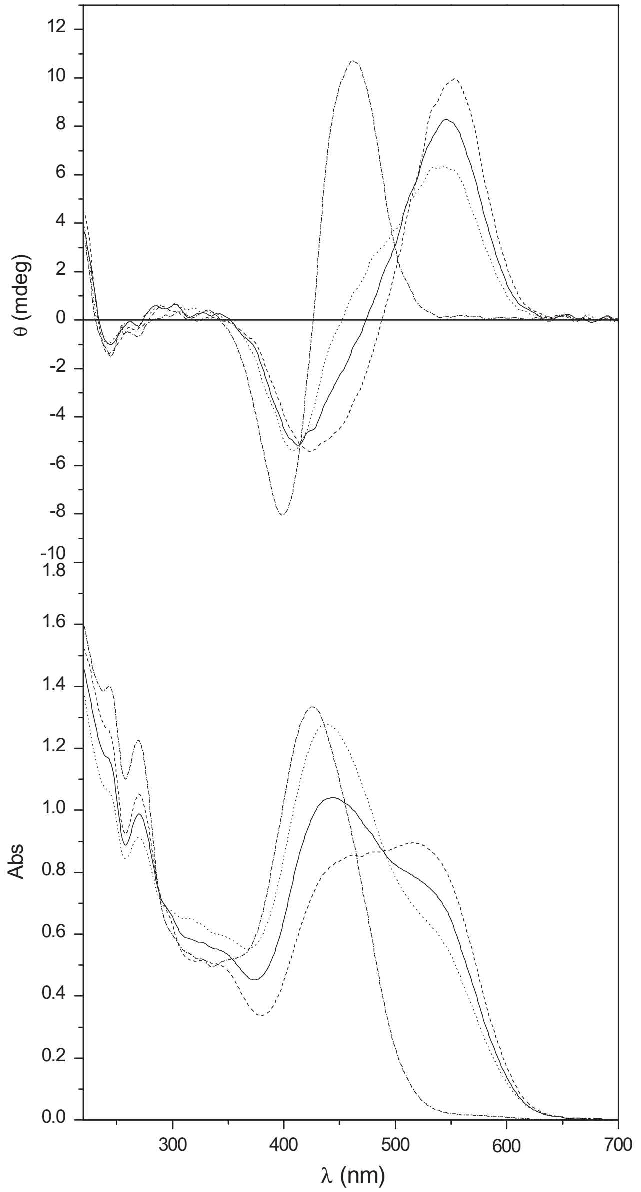


Fig. 7. UV–Vis (bottom) and CD spectra (top) of a solution of poly[(*S*,*S*)-**MLL-SP**] and poly[(*S*)-**AZ**] 1:1 in dichloroethane (5×10^{-4} M) (-·-·-), in the presence of one equivalent of TFA (- - -), upon irradiation at 365 nm (···) and at 436 nm (—).

investigate their photochromic properties by chiroptical methods, also, in addition to be of interest in the field of the chiral nanotechnology, and to investigate the amplification of chirality in polymeric materials.

3.4. Photoresponsive properties and photomodulation of proton transfer between azopyridine and spiropyran dyes

The literature reports the possibility to photo-modulate the proton transfer between low molecular weight spiropyran and azopyridine systems in solution [20,24]. Recently, it was demonstrated that the same process can also take place when these functionalities are bonded to distinct macromolecular chains [25] or to the same macromolecular chain in copolymeric derivatives [35].

Moreover, the insertion of a pyrrolidine group of one prevailing configuration between the polymeric backbone and the *trans*-azopyridine dye allows to monitor the reversible and reproducible signal communication by CD, as well as by UV–Vis spectroscopy.

In this context, solutions of the investigated chiral spiropyran polymeric materials containing an equimolar amount of azopyridine homopolymer {poly[(*S*)-**AZ**]} have been irradiated alternatively by UV and Visible light in the presence of one equivalent of TFA, affording the protonated form {poly[(*S*)-**AZH**]}. All the derivatives displayed a UV–Vis behavior similar to that previously reported for the mixture of the corresponding homopolymers poly[**M-SP**] and poly[(*S*)-**AZ**] [25].

As shown in Fig. 7 (bottom) for poly[(*S*,*S*)-**MLL-SP**] and poly[(*S*)-**AZH**], in fact, upon irradiation at 365 nm, the spiropyran moiety isomerizes to the open form [(*S*,*S*)-**ME**], which deprotonates (*S*)-**AZH** to give the (*S*,*S*)-**MLL-MEH** and (*S*)-**AZ** species. Such behavior is consistent with the absorption spectra changes: the absorption bands around 270 and 540 nm, related to (*S*,*S*)-**MLL-SP** and (*S*)-**AZH** species, respectively, decrease, while that one at 425 nm, due to (*S*,*S*)-**MLL-MEH** and (*S*)-**AZ**, increases in intensity. The back isomerization of (*S*,*S*)-**MLL-MEH** to (*S*,*S*)-**MLL-SP** is obtained by irradiation at 436 nm, thus inducing again the proton transfer to (*S*)-**AZ**. As a result, the absorption band related to merocyanine decreases, while those around 270 and 540 nm increase again.

This process is reproducible and reversible: by submitting the materials to several cycles of UV and Visible photoirradiation, in fact, it is possible to tune the absorbance at a specific wavelength (e.g. at 460 nm, as shown in the inset of Fig. 8 (bottom) for poly[(*S*,*S*)-**MLL-SP**]), with a good fatigue resistance. Indeed, after several irradiations steps with UV and Vis light alternatively acting on the same solution, the values of absorbance remain quite similar. This indicates that no degradation photoreactions or relevant variation of interchromophoric interactions take place.

Thus, several photoinduced cycles could be performed without any significant change in the proton-transfer behavior.

The above described photoinduced changes in the absorption spectra are accompanied by changes of dichroic signals. As reported in Fig. 7 (top), the 1:1 mixture of poly[(*S*,*S*)-**MLL-SP**] and poly[(*S*)-**AZ**] displays, upon addition of one equivalent of TFA, a CD spectrum very similar to that one of the homopolymer poly[(*S*)-**AZH**] alone [25]. In fact, in addition to a weak positive band around 270 nm related to the π–π* electronic transition, two intense dichroic signals of opposite sign and similar intensity, with a cross-over point in correspondence of the first UV maximum absorbance (at about 490 nm), related to the chiral (*S*)-**AZH** moieties, are displayed. Low intensity signals in the spectral range 220–270 nm, related to the chiral (*S*,*S*)-**MLL-SP** moieties, are also present.

As exhaustively discussed in the literature [25], the excitonic splitting of the azoaromatic electronic transitions is typical of methacrylic azobenzene polymers bearing in the side chain the optically-active (*S*)-3-hydroxy pyrrolidinyl group of one single configuration [37] and suggests the presence of cooperative interactions between side-chain azopyridine chromophores disposed in a mutual chiral geometry of one prevailing helicity.

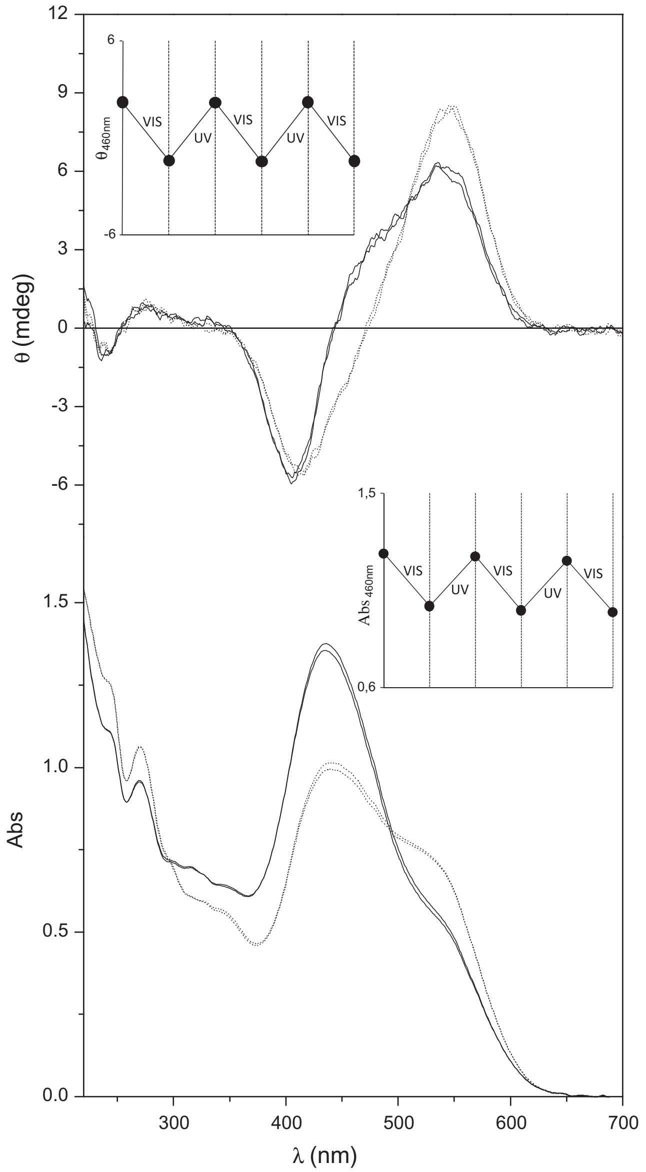


Fig. 8. Photochromic modulation of absorbance intensity (bottom) and ellipticity intensity (top) of a solution of poly[(*S*,*S*)-**MLL-SP**] and poly[(*S*)-**AZ**] 1:1 in dichloroethane (5×10^{-4} M) in the presence of one equivalent of TFA under irradiation at 365 nm (—) and at 436 nm (···). Inset: intensity variation at 460 nm of the UV and CD spectra measured upon alternating irradiation at 365 (UV) and 436 (Vis) nm.

By irradiating this solution at 365 nm, the formation of the merocyanine state is promoted, with proton transfer from the (*S*)-**AZH** to the (*S*,*S*)-**MLL-ME** form, with a consequent noticeable change in the position and shape of the CD bands related to the (*S*)-**AZ**/(*S*)-**AZH** ratio. However, the shape and intensities of the CD signals in the spectral range 220–300 nm are practically unaffected by proton-transfer phenomena during the photoisomerization, and hence the process can be followed by observing the CD variations connected to the more intense transitions of the azopyridine chromophore.

The back isomerization is promoted by irradiation with Visible light and, as a result, the CD bands related to the protonated (*S*)-**AZH** form increase again. This phenomenon is reversible and the system does not show any degradation after several irradiation cycles (see inset in Fig. 8, top).

As expected, the homopolymer with only one chiral residue of lactic acid {poly[(*S*)-**ML-SP**]} shows a similar behavior as poly[(*S*,*S*)-**MLL-SP**] when irradiated in the presence of poly[(*S*)-**AZ**] and TFA.

In conclusion, the present investigation shows the possibility to tune the protonation of the azopyridinic group by controlling the photoisomerization of intrinsically chiral spiropyran moieties when these groups are bonded to a distinct macromolecular chain, also.

4. Conclusions

Novel homopolymeric methacrylates bearing in the side chains the optically-active L-lactic acid residue linked to the spiropyran chromophore were prepared by radical polymerization of the corresponding monomers.

Thermal analysis shows the presence of remarkable interaction between neighboring spiropyran moieties related to the flexibility of the side-chain chiral spacer.

The CD spectra of these macromolecular materials in solution are characterized by enhanced dichroic signals related to the electronic transitions of the spiropyran chromophores with respect to the monomers. The polymers display remarkable reversible changes of their photochromic properties evidenced by UV–Vis measurements in response to environmental stimuli. In particular, when these systems are mixed in solution with an optically active methacrylate homopolymer bearing in the side chain the azopyridine chromophore, in the presence of acid, a modulation of azopyridine protonation by photo-isomerization of the spiropyran component can be achieved. The signal communication between these polymeric switches can be monitored by UV–Vis as well as CD spectroscopy, and is completely reversible and reproducible.

The chemical anchorage of spiropyran photochromic molecules to polymeric matrices thus allows the combination of their intrinsic photochemical properties with those typical of polymers, such as processability and stability.

Acknowledgements

Financial support from Consortium INSTM and University of Bologna (Marco Polo Program) are gratefully acknowledged.

References

[1] T. Kajitani, K. Okoshi, S. Sakurai, J. Kumaki, E. Yashima, J. Am. Chem. Soc. 128 (2006) 708–709.
[2] E. Yashima, K. Maeda, T. Nishimura, Chem. Eur. J. 10 (2004) 42–51.
[3] A.J. Wilson, M. Masuda, R.P. Sijbesma, E.W. Meijer, Angew. Chem. Int. Ed. 44 (2005) 2275–2279.

[4] M.M. Green, N.C. Peterson, T. Sato, A. Teramoto, R. Cook, S. Lifson, Science 268 (1995) 1860–1866.
[5] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, A. Altomare, C. Carlini, R. Solaro, Polymer 41 (2000) 4767–4780.
[6] L. Angiolini, T. Benelli, L. Giorgini, F. Mauriello, E. Salatelli, Macromol. Chem. Phys. 207 (2006) 1805–1813.
[7] L. Angiolini, T. Benelli, L. Giorgini, Polymer 52 (2011) 2747–2756.
[8] C. Carlini, L. Angiolini, D. Caretti, Photochromic optically active polymers, in: J.C. Salomone (Ed.), Polymeric Materials Enciclopedia, vol. 7, CRC Press, Boca Raton, 1996, pp. 5116–5123.
[9] J. Zhang, T. Albelda, Y. Liu, J.W. Canary, Chirality 17 (2005) 404–420.
[10] M.M. Green, R.J.M. Nolte, E.W. Meijer, S.E. Denmark, J. Siegel, Topics in Stereochemistry: Materials-Chirality, vol. 24, Wiley VCH, New York, 2003.
[11] G.S. Kumar, D.C. Neckers, Chem. Rev. 89 (1989) 1915–1925.
[12] P.N. Prasad, D.J. Williams, Introduction to Linear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
[13] D.M. Burland, R.D. Miller, C.A. Walsh, Chem. Rev. 94 (1994) 31–75.
[14] C.B. McArdle (Ed.), Applied Photochromic Polymer Systems, Blackie, London, 1992.
[15] R. Bertelson, in: G.H. Brown (Ed.), Photochromism, vol. 45, Wiley, New York, 1971.
[16] Y. Hirshberg, Compt. Rend. Acad. Sci. Paris 231 (1950) 903–904.
[17] Y. Hirshberg, E. Fischer, J. Chem. Soc. (1953) 629–636.
[18] G. Berkovic, V. Krongauz, V. Weiss, Chem. Rev. 100 (2000) 1741–1753.
[19] F.M. Raymo, S. Giordani, J. Am. Chem. Soc. 124 (2002) 2004–2007.
[20] F.M. Raymo, S. Giordani, Org. Lett. 3 (2001) 3475–3478.
[21] X. Guo, D. Zhang, G. Yu, M. Wan, J. Li, Y. Liu, D. Zhu, Adv. Mater. 16 (2004) 636–640.
[22] R. Guglielmetti, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990. pp. 314–466, 855–878.
[23] R.C. Beterlson, in: J.C. Crano, R. Guglielmetti (Eds.), Organic Photochromic and Thermochromic Compounds, Plenum Press, New York, 1999, pp. 11–83.
[24] S. Giordani, M.A. Cejas, F.M. Raymo, Tetrahedron 60 (2004) 10973–10981.
[25] L. Angiolini, T. Benelli, L. Giorgini, F.M. Raymo, Macromol. Chem. Phys. 209 (2008) 2049–2060.
[26] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Adv. Mater. 11 (1999) 1025–1028.
[27] J.S. Moore, S. Stupp, Macromolecules 23 (1990) 65–70.
[28] D.D. Perrin, W.L.F. Amarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1966.
[29] F.M. Raymo, S. Giordani, J. Am. Chem. Soc. 123 (2001) 4651–4652.
[30] V.A. Miller, R.R. Brown Jr., E.B. Gienger, US Pat. 3 067 180, 1962.
[31] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, A. Altomare, C. Carlini, R. Solaro, Polymer 39 (1998) 6621–6629.
[32] L. Angiolini, D. Caretti, C. Carlini, L. Giorgini, E. Salatelli, Macromol. Chem. Phys. 200 (1999) 390–398.
[33] F.M. Raymo, R.J. Alvarado, S. Giordani, M.A. Cejas, J. Am. Chem. Soc. 125 (2003) 2361–2364.
[34] J.H. Kim, S.Y. Ban, S. Kaihua, D.H. Choi, Dyes Pigm. 58 (2003) 105–112.
[35] L. Angiolini, T. Benelli, L. Giorgini, F.M. Raymo, Polymer 50 (2009) 5638–5646.
[36] M. Sakuragi, K. Aoki, T. Tamaki, K. Ichimura, Bull. Chem. Soc. Jpn. 63 (1990) 74–79.
[37] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 3257–3268.