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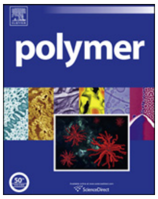

Optical and chiroptical switches based on photoinduced photon and proton transfer in copolymers containing spiropyran and azopyridine chromophores in their side chains

L. Angiolini [a,*], T. Benelli [a], L. Giorgini [a], F.M. Raymo [b]

[a] Dipartimento di Chimica Industriale e dei Materiali and INSTM UdR-Bologna, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy
[b] Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, FL 33146-0431, USA

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ABSTRACT

New methacrylic copolymers, bearing in the side chain spiropyran moieties and/or the optically-active (*S*)-3-hydroxy pyrrolidinyl group linked through the nitrogen atom to an azopyridine chromophore, along with an opportune molar content of methyl methacrylate co-units, have been prepared by radical polymerization of the corresponding monomers.

The resulting macromolecules have been fully characterized with particular attention to the study of their thermal stability, optical activity, chiroptical and photoinduced properties.

In the presence of acid, it is possible to modulate the protonation of the azopyridine groups by photoisomerization (with UV and/or Vis light) of the spiropyran component. The resulting signal communication between these macromolecular switches can be monitored by UV–VIS as well as CD spectroscopy and is completely reversible and reproducible.

The results are discussed in terms of copolymer composition and different cooperative behaviour, which lead to a variation of interactions between spiropyran and azoaromatic chromophores and reveal that the best proton transfer is actually obtained in the random terpolymer with lower amounts of *co*-units of spiropyran and azopyridine chromophores in the side chain, which displays improved sensitivity to proton-transfer process and, in addition, exhibits good stability to repeated cycles of irradiation with UV and Vis light.

1. Introduction

In the last few years a considerable interest has grown up in the study of molecular switches: molecules undergoing reversible transformations in response to chemical, electrical and/or optical stimulations [1–4]. Under the influence of suitable input stimulations, these chemical systems switch from one form to another producing a change in a detectable output [5–8], being of remarkable potential interest for several technological applications, such as devices for the optical storage of informations, optical switches, chemical photoreceptors and, in general, as materials exhibiting photoresponsive properties when irradiated with light of suitable frequency and intensity [9–11].

In this regard, the reversible isomerization of certain spiropyran derivatives, upon external light or chemical stimulations, has been widely investigated [5–8,12–15].

It is well known that the colorless spiropyran (**SP**), upon irradiation with ultraviolet (UV) light, isomerizes to the purple merocyanine form (**ME**) through heterolytic cleavage of the spiro carbon–oxygen bond. The process is thermally and photochemically reversible. Furthermore the photogenerated opened form **ME**, after addition of acid, switches completely to the protonated merocyanine species (**MEH**) which, if irradiated with Visible (VIS) light, releases a proton and switches back to **SP**. The absorption and emission properties of these three states (**SP**, **ME** and **MEH**) are significantly different and allow to use these compounds for repeated data recording and optical data storage [5–8,12–15].

Fascinating strategies to implement memory devices based on these photochromic compounds have recently been proposed, such as the intermolecular communication between different molecular switches based on photon and/or proton transfer [7,8,16].

In this context we have just reported the possibility to couple in blend homopolymeric methacrylic spirobenzopyran systems, poly[1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline)] {poly[**SP**]}, with a polymer functionalized with chiral azopyridine moieties, poly[(*S*)-3-methacryloyloxy-1-[4-(2-pyridilazo)phenyl] pyrrolidine] {poly[(*S*)-**AZ**]}

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[*] Corresponding author. Tel./fax: +39 051 2093687.
E-mail address: luigi.angiolini@unibo.it (L. Angiolini).

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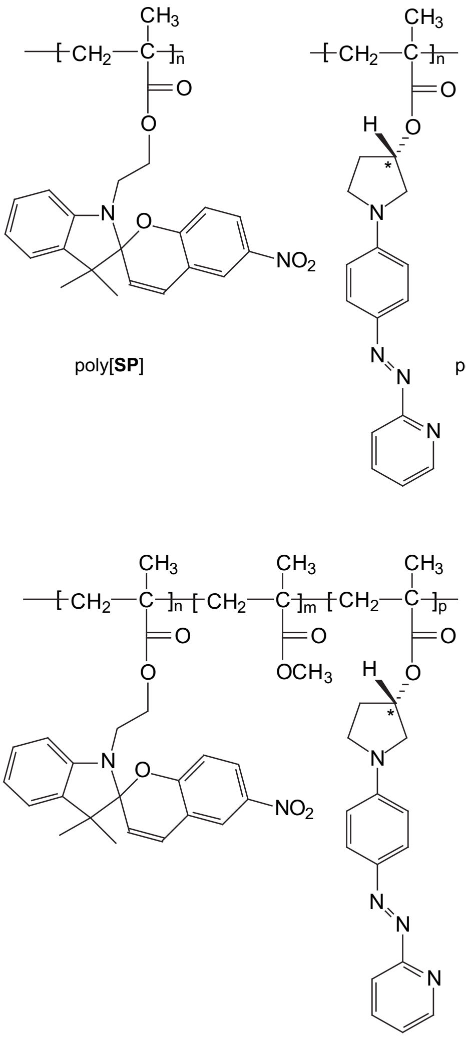
[17] (Fig. 1), which can exist in the unprotonated (poly[(*S*)-**AZ**]) and protonated form (poly[(*S*)-**AZH**]).

It was demonstrated that the release of the proton by the azopyridine compound can be modulated by controlling the interconversion between **SP** and **ME** by UV and VIS light [8,16,17] and that the obtained signal communication between these polymeric switches can be monitored not only by UV–VIS spectroscopy, but also by circular dichroism (CD) [17], due to the presence of achiral group of one prevailing configuration interposed between the polymeric backbone and the *trans*-azopyridine chromophore. This functional combination allows the polymers to display the properties typical of dissymmetric systems (optical activity, exciton splitting of chiroptical absorptions) and it is considered of interest in the field of the chiral nanotechnology [18,19] and to investigate the amplification of chirality of polymeric materials [20–22].



poly[**SP**-*co*-(*S*)-**AZ**] 1:1	n=0.46	m=0	p=0.54
poly[**SP**-*co*-**MMA**] 1:19	n=0.04	m=0.96	p=0
poly[(*S*)-**AZ**-*co*-**MMA**] 1:19	n=0	m=0.95	p=0.05
poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18	n=0.06	m=0.88	p=0.06
poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8	n=0.16	m=0.74	p=0.10

Fig. 1. Molecular structures of the polymers.

With the aim to obtain a more effective photoinduced proton transfer between the chromophores, we envisaged the possibility to combine both azopyridine and spiropyran moieties in the same macromolecular chain (Fig. 1) by radical copolymerization of the corresponding methacrylic monomers [(*S*)-3-methacryloyloxy-1-[4-(2-pyridilazo)phenyl] pyrrolidine] [(*S*)-**AZ**] and 1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline) [**SP**].

Furthermore, with the aim to evaluate the effects induced on the properties of these materials by progressively spacing out the photochromic repeating units along the polymeric backbone, in addition to the copolymer with the same molar amount of chromophores (Poly[**SP**-*co*-(*S*)-**AZ**] 1:1), we have prepared several terpolymers with different amounts of methyl methacrylate *co*-units (Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8 and 1:1:18) and, as reference models, the copolymers poly[**SP**-*co*-**MMA**] 1:19 and poly[(*S*)-**AZ**-*co*-**MMA**] 1:19 (Fig. 1).

These new chiral polymeric materials have been characterized by common spectroscopic techniques with particular attention to their chiroptical and photoresponsive properties.

2. Experimental section

2.1. Physico–chemical measurements

^{1}H and ^{13}C NMR spectra were obtained at room temperature, in 5–10% $CDCl_3$ solutions, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). ^{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 recorded with a Perkin-Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station, on sample prepared as KBr pellets.

Number average molecular weights of the polymers ($\overline{M}_n$) and their polydispersity indexes ($\overline{M}_w/\overline{M}_n$) were determined in THF solution by SEC using a 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. The calibration curve for the MXL column was obtained by using monodisperse polystyrene standards in the range 800–35,000.

The glass transition temperatures of the polymers (T_g) were determined by differential scanning calorimetry (DSC) on a TA Instruments 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 a nitrogen atmosphere). Each sample (5–9 mgr) was heated up to only 250 °C in order to avoid thermal decomposition.

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.

UV–VIS absorption spectra in solution were recorded at 25 °C in $C_2H_4Cl_2$ with a Varian Cary 100 Bio spectrophotometer. The spectral region 800–220 nm was investigated by using cells with a path length of 0.5 cm. In all cases, sample concentrations of about 5.0×10^{-4} mol L^{-1} refers to azopyridine chromophores were used.

Circular dichroism (CD) spectra were recorded at 25 °C in dichloroethane solutions on a Jasco 810 A dichrograph, using cells with a path length of 0.1 cm and solution concentrations of about 5.0×10^{-4} mol L^{-1}. $\Delta\epsilon$ values, expressed as L mol^{-1} cm^{-1}, were calculated from the following expression: $\Delta\epsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg cm^2 d mol^{-1} refers to one azopyridine chromophore.

Irradiations experiments at 365 nm were carried out at 25 °C in dichloroethane solution (2 ml using the same cells and solution concentrations of the UV–VIS and CD measurements), using a Mineralight UVGL-25 lamp.

Irradiations at 436 nm were carried out under 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.

3. Materials

The azopyridine monomer (*S*)-3-methacryloyloxy-1-[4-(2-pyridylazo)phenyl] pyrrolidine [(*S*)-**AZ**] and the spiropyran monomer 1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline) [**SP**] were synthesized as previously reported [17].

MMA (Aldrich) was distilled at reduced pressure under nitrogen atmosphere in the presence of traces of 2,6-di-*tert*-butyl-*p*-cresol as polymerization inhibitor before use [23].

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

Tetrahydrofuran (THF) and dichloroethane (DCE), were purified and dried according to reported procedures [23] and stored over molecular sieves (4 Å) under nitrogen.

All other reagents and solvents (Aldrich) were used as received.

3.1. General procedure for free radical polymerization

All copolymerization reactions involving (*S*)-**AZ**, **SP** and **MMA** were carried out in glass vials using AIBN as thermal initiator (2 wt% with respect to the monomers) and dry THF as solvent (1 g of monomers in 15 ml of THF). Feeds of molar composition, as reported in Table 1, were introduced into the vials under nitrogen atmosphere, submitted to several freeze-thaw cycles, and allowed to polymerize at 60 °C for 72 h. Polymerizations were then stopped by pouring the mixtures into a large excess of methanol and the polymeric products purified by repeated precipitations in methanol or petroleum ether. The materials were finally dried at 80 °C for 4 days under high vacuum to constant weight. The conversions were determined gravimetrically and all the products were characterized by FT-IR, ^{1}H and ^{13}C NMR.

*Poly[(S)-**AZ**-co-**SP**] 1:1*

^{1}H NMR (CDCl$_3$): 8.75–8.50 (m, 1H, arom. pyridine 6-H), 8.10–7.55 (m, 6H, 4H arom. *metha* to amino group and arom. pyridine 3- and 4-H; 2H, arom. *ortho* to nitro group), 7.35–6.30 (m, 9H, 3H arom. pyridine 5-H and 2H, and arom. *ortho* to amino group; 5H, arom. indoline and 1H C*H*=CH–CO), 5.90–5.60 (m, 1H, CH=C*H*–CO), 5.40–4.70 (m, 1H, CH–O), 4.20–3.75 (m, 2H, CH$_2$–O), 3.75–3.00 (m, 6H, 4H, pyrrolidine 2- and 5-CH$_2$; 2H, CH$_2$–N of **SP**), 2.30–0.50 (m, 18H, pyrrolidine 4-CH$_2$, indoline 2CH$_3$, and backbone CH$_3$ and CH$_2$) ppm.

FT-IR (KBr) (cm^{-1}): 3049 (ν_{CH}, arom.), 2963 (ν_{CH}, aliph.), 1726 ($\nu_{C=O}$, ester), 1602 and 1516 ($\nu_{C=C}$, arom.), 1140 ($\nu_{C\text{-}O}$), 819 and 744 (δ_{CH} arom.) cm^{-1}.

*Poly[**SP**-co-**MMA**] 1:19*

^{1}H NMR (CDCl$_3$): 8.10–8.00 (m, 2H, arom. *ortho* to nitro group), 7.25–6.60 (m, 6H, 5H arom. indoline and 1H C*H*=CH–CO), 5.95–5.85 (m, 1H, arom. CH=C*H*–CO), 4.20–4.00 (m, 2H, CH$_2$–O), 3.80–3.30 (m, 5H, 2H, CH$_2$–N and 3H, **MMA** OCH$_3$), 2.10–0.60 (m, 16H, indoline 2CH$_3$, and backbone CH$_3$ and CH$_2$) ppm.

FT-IR (KBr): 3040 (ν_{CH}, arom.), 2950 (ν_{CH}, aliph.), 1728 ($\nu_{C=O}$, ester), 1611 and 1523 ($\nu_{C=C}$, arom.), 1147 ($\nu_{C\text{-}O}$), 807 and 749 (δ_{CH} arom.) cm^{-1}.

*Poly[(S)-**AZ**-co-**MMA**] 1:19*

^{1}H NMR (CDCl$_3$): 8.70–8.60 (m, 1H, arom. pyridine 6-H), 8.10–7.95 (m, 2H, arom. *metha* to amino group), 7.90–7.70 (m, 2H, arom. pyridine 3-H and 4-H), 7.35–7.25 (m, 1H, arom. pyridine 5-H), 6.70–6.55 (m, 2H, arom. *ortho* to amino group), 5.40–5.25 (m, 1H, CH–O), 3.80–3.35 (m, 4H, pyrrolidine 2- and 5-CH$_2$ and 3H, **MMA** OCH$_3$), 2.35–2.20 (2H, pyrrolidine 4-CH$_2$), 2.10–0.70 (m, 10H, backbone CH$_3$ and CH$_2$) ppm.

FT-IR (KBr): 3045 (ν_{CH}, arom.), 2950 (ν_{CH}, aliph.), 1725 ($\nu_{C=O}$, ester), 1602 and 1516 ($\nu_{C=C}$, arom.), 1142 ($\nu_{C\text{-}O}$), 824 and 749 (δ_{CH} arom.) cm^{-1}.

*Poly[(S)-**AZ**-co-**SP**-co-**MMA**] 1:1:18 and 1:1:8*

^{1}H NMR (CDCl$_3$): 8.75–8.65 (m, 1H, arom. pyridine 6-H), 8.10–7.95 (m, 2H arom. in *ortho* to nitro group), 7.90–7.75 (4H, arom. *metha* to amino group and arom. pyridine 3-H and 4-H), 7.35–6.55 (m, 9H, 3H arom. pyridine 5-H and 2H arom. *ortho* to amino group; 5H, arom. indoline and 1H C*H*=CH–CO), 5.96–5.85 (m, 1H, CH=C*H*–CO), 5.35–5.20 (m, 1H, CH–O), 4.20–3.95 (m, 2H, CH$_2$–O), 3.80–3.30 (m, 9H, 4H pyrrolidine 2- and 5-CH$_2$; 2H, CH$_2$–N of **SP**, 3H, **MMA** OCH$_3$), 2.35–2.20 (2H, pyrrolidine 4-CH$_2$), 2.10–0.60 (m, 21H, indoline 2CH$_3$, and backbone CH$_3$ and CH$_2$) ppm.

FT-IR (KBr): 3048 (ν_{CH}, arom.), 2949 (ν_{CH}, aliph.), 1730 ($\nu_{C=O}$, ester), 1603 and 1518 ($\nu_{C=C}$, arom.), 1143 ($\nu_{C\text{-}O}$), 818 and 751 (δ_{CH} arom.) cm^{-1}.

Table 1
Characterization data of polymeric derivatives.

Feed in mol%			Final composition in mol%			Yield[a] %	$\overline{M}_n$[b] (g/mol)	$\overline{M}_w/\overline{M}_n$ [b]	T_g (°C)[c]	T_d (°C)[d]
SP	(*S*)-**AZ**	**MMA**	**SP**	(*S*)-**AZ**	**MMA**					
50	50	–	46	54	–	52	5600	1.5	169	248
5	–	95	4	–	96	52	9100	2.0	105	257
–	5	95	–	5	95	45	13,600	1.6	115	256
5	5	90	6	6	88	73	11,200	1.8	124	255
10	10	80	16	10	74	51	8900	1.8	125	246
100[e]	–	–	100[e]	–	–	73[e]	11,800[e]	1.8[e]	166[e]	275[e]
–	100[e]	–	–	100[e]	–	75[e]	15,800[e]	1.6[e]	164[e]	241[e]

[a] Calculated as (g of polymer/g of monomer)·100.
[b] Determined by SEC in THF at 25 °C.
[c] Determined by DSC.
[d] Determined by TGA.
[e] Ref. [17].

4. Results and discussion

4.1. Synthesis and characterization

The copolymerizations of (*S*)-**AZ** and/or **SP** and/or with **MMA** in different molar amounts were carried out in THF solution under radical conditions in the presence of AIBN as thermal initiator. Relevant data for the synthesized derivatives are reported in Table 1 and compared with the previously investigated homopolymers Poly[(*S*)-**AZ**] and Poly[**SP**] [17].

The occurrence of polymerization involving the methacrylic double bond was confirmed by FT-IR, showing the disappearance of the band around 1630 cm^{-1}, which corresponds to the stretching vibration of the double bond in the monomers, and the shift of the estereal carbonyl stretching to higher frequencies as a result of the reduced electron delocalization caused by the reaction of the methacrylic double bond.

Accordingly, in the ^{1}H NMR spectra of the polymers, the resonances of the vinylic protons of monomeric methacrylate (around 5.60 and 6.10 ppm) are absent and the methyl resonances are shifted to higher field.

The final molar composition of the obtained copolymers (Table 1), as assessed by ^{1}H NMR by comparing the integrated peak areas of the different *co*-units in both the aromatic and aliphatic regions, results to reflect the feed composition. Such a behaviour points out a similar reactivity of the different monomers.

As shown by SEC analysis, the polydispersity indexes (Table 1) of all the obtained derivatives result similar and in the range 1.6–2.0, values typical of free radical polymerization. However, the contemporary presence of sterically hindered spiropyran and azopyridine dyes seems to affect the polymerization extent. By increasing the amount of MMA *co*-units, in fact, the number average molecular weight of the obtained derivatives increases (Table 1), probably due to their lower steric hindrance with respect to the other two chromophores. The benzopyran derivative, in particular, appears to negatively affect the process, because of the presence of the aromatic nitro moiety which is known to affect greatly the radical polymerization [24], thus favouring an increased extent of transfer and termination reactions. This is confirmed by the lower number average molecular weight ($\overline{M}_n$) shown by poly[**SP**] in comparison with poly[(*S*)-**AZ**] obtained under the same condition [17] (Table 1).

The dried polymeric samples resulted soluble in the usual solvents (THF and $CHCl_3$) commonly employed for methacrylic polymers as well as in strongly polar solvents such as nitrobenzene, DMF, DMA or dimethylsulfoxide (DMSO).

The thermal stability of all the polymeric derivatives was determined by thermogravimetric analysis (TGA).

The quite similar decomposition temperature (T_d) values obtained for all copolymeric derivatives resulted appreciably high, in the range of 245–255 °C, indicative of an appreciable thermal stability of the macromolecules under the adopted conditions.

DSC thermograms of the investigated copolymers (Table 1) revealed only second-order transitions originated by glass transitions, with no melting peaks, thus suggesting that these macromolecules are substantially amorphous in the solid state. The T_g value of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 appears quite high and similar to those one of the corresponding homopolymers (around 165 °C). This behaviour can be ascribed to the stiffness and steric hindrance of the spiropyran group and to the presence of dipolar inter- and intra-molecular interactions between azopyridine chromophores, as previously reported for analogous methacrylic systems binding azoaromatic groups in the side chain [25].

The insertion of MMA *co*-units, instead, increases the chain flexibility, as demonstrated by the decrease of the T_g values. However, it can be noted that even the samples containing the smallest amount of azoaromatic and/or spiropyran co-units display a higher T_g value than that one reported for poly(**MMA**) (104 °C) [26], thus confirming the presence of strong inter- and/or intramolecular dipolar interactions in the solid state between chromophores

Table 2
UV–VIS spectra of polymeric compounds and their corresponding monomers in dichloroethane solution at 25 °C.

Samples	1st band		2nd band		3rd band		4th band	
	λ_{max}[a]	ε_{max}[b]	λ_{max}[a]	ε_{max}[b]	λ_{max}[a]	ε_{max}[b]	λ_{max}[a]	ε_{max}[b]
SP[c]	–	–	341	8700	268	16,400	243	20,200
Poly[**SP**][c]	–	–	341	8100	269	16,200	243	20,100
Poly[**SP**-*co*-**MMA**] 1:19	–	–	339	8000	267	16,300	243	19,600
(*S*)-**AZ**[c]	425	31,800	–	–	269	9700	–	–
Poly[(*S*)-**AZ**][c]	424	23,700	–	–	270	8300	–	–
Poly[(*S*)-**AZ**-*co*-**MMA**] 1:19	427	28,600	–	–	270	8100	–	–
Poly[**SP**-*co*-(*S*)-**AZ**] 1:1	425	29,400[d]	–	–	268	n.d.[e]	245	n.d.[e]
Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18	427	29,500[d]	–	–	269	n.d.[e]	245	n.d.[e]
Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8	427	26,700[d]	–	–	269	n.d.[e]	244	n.d.[e]

[a] Wavelength of maximum absorbance, expressed in nm.
[b] Expressed in $L \cdot mol^{-1} \cdot cm^{-1}$ and calculated for one single chromophore.
[c] Ref. [17].
[d] Calculated by (*S*)-**AZ** concentration.
[e] Not determined due to the overlapping of the **SP** and (*S*)-**AZ** absorbance contribution.

4.2. UV–VIS and photochromic properties

In analogy to other spiropyran derivatives [8,16,27], copolymer poly[**SP**-co-**MMA**] 1:19 shows, in 1,2-dichloroethane solution, three absorption bands below 400 nm: the first one, located at 339 nm, is related to the internal charge transfer transition of the spiropyran system; the other two, at 267 and 243 nm, more intense, to the electronic transitions of the single aromatic ring (Table 2 and Fig. 2).

On the other hand, poly[(*S*)-**AZ**-*co*-**MMA**] displays a spectrum very similar to the corresponding homopolymer poly[(*S*)-**AZ**] and monomer (*S*)-**AZ** [17], with two absorption bands: the former, more intense, located at 425 nm, is related to the n–π^*, π–π^* and internal

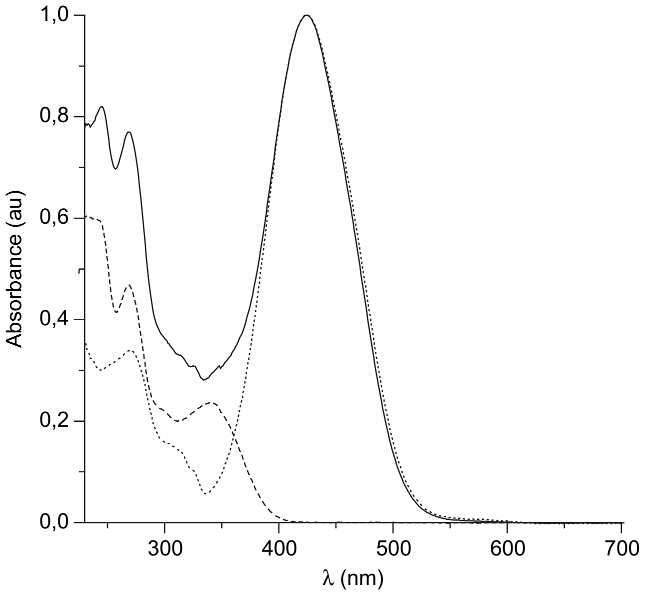


Fig. 2. UV–vis spectra of poly[**SP**-*co*-**MMA**] 1:19 (- - -), poly[(*S*)-**AZ**-*co*-**MMA**] 1:19 (···), and poly[**SP**-*co*-(*S*)-**AZ**] 1:1 (—) in dichloroethane solution.

charge transfer electronic transitions of the conjugated azopyridine chromophore; the latter, centred at 270 nm, is related to the π–π^* electronic transition of the aromatic ring [28] (Table 2 and Fig. 2).

Thereby copolymers bearing in the side chain both chromophoric dyes (Poly[**SP**-*co*-(*S*)-**AZ**] 1:1 and Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8 and 1:1:18), exhibit UV–VIS absorption spectra which are the sum of their components (Table 2 and Fig. 2).

A significant hypochromism was formerly observed for both the first and the second band when passing from the monomer (*S*)-**AZ** to the corresponding polymer poly[(*S*)-**AZ**] [17] (Table 2). Such behaviour, previously observed in several macromolecular compounds bearing side-chain azoaromatic chromophores [29–31], was attributed to the occurrence of electrostatic dipole-dipole interactions between the neighbouring aromatic groups [32–34].

By increasing the distance between azopyridine dyes through the insertion of non-chromophoric methacrylic *co*-units (Poly[(*S*)-**AZ**-*co*-**MMA**] 1:19), a lower amount of intramolecular dipolar interactions is present, which gives rise to an increase of the molar absorption coefficient ϵ_{max} (Table 2). This effect becomes more evident by inserting, in the same macromolecular chain, sterically hindered spiropyran *co*-monomers (Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8 and 1:1:18) which disfavoured mutual interactions between azopyridine moieties.

With the aim to establish if the integration of spiropyran and azopyridine functionalities in the same chain allows to maintain the properties of both of them, the synthesized compounds have been irradiated with UV and Visible light and treated with trifluoroacetic acid (TFA).

By irradiating the diluted solution of spiropyran functionalized materials at 365 nm, the system isomerizes to the merocyanine form (**ME**) because of the cleavage of C–O bond. Thus, the conjugation between the aromatic rings increases, and an absorption band at 575 nm related to the merocyanine π–π^* transitions appears (Fig. 3).

All the synthesized copolymers show the same behaviour, but the intensity of the merocyaninic band at the stationary state, on equal terms of concentration and irradiation time, is strongly different. 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] [35], it has been possible to evaluate the amount of **ME** (ME%) in each polymeric derivative at the photostationary state, after irradiation with UV light. The obtained data show that the insertion of azopyridine unit slows down the spiropyran isomerization process, resulting in a lower amount of open form in poly[**SP**-*co*-(*S*)-**AZ**] 1:1 with respect to poly[**SP**] after the same irradiation time (15% and 30% respectively). The further insertion of methacrylic *co*-units gives rise to an additional decrease of isomerization, thus terpolymers poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8 and 1:1:18 (8 and 9% of ME% form, respectively) display a behaviour similar to the monomer **SP** (9% of ME% form).

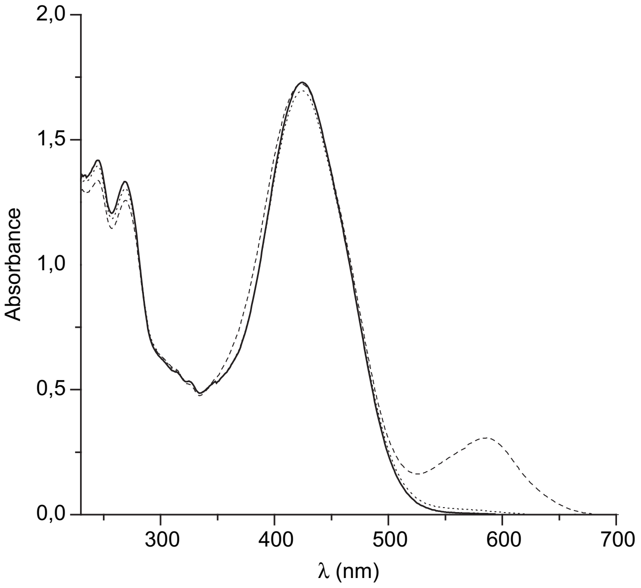


Fig. 3. UV–vis spectra of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 in dichloroethane before (—) and after irradiation at 365 nm (- - -) and after subsequent irradiation at 436 nm (···).

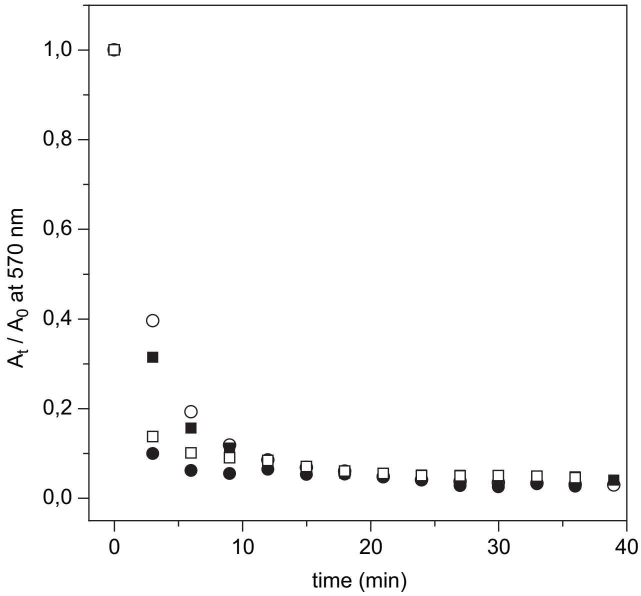


Fig. 4. UV–vis absorbance values expressed as A_t/A_0 (at 570 nm) of poly[**SP**] (○), poly[**SP**-*co*-(*S*)-**AZ**] 1:1 (■), poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 (□), and monomer **SP** (●) at 25 °C in dichloroethane solution stored in the dark after irradiation at 365 nm.

Such a behaviour can be ascribed to the occurrence of lower dipolar interactions between spiropyran chromophores in the side chain which can stabilize the merocyanine form, and which fade by increasing the distance between them. This hypothesis is confirmed by the different spiropyran back-isomerization rates of the solutions stored in the dark. In these conditions the merocyaninic residue back isomerizes to the neutral closed form **SP** which is thermodynamically more stable. By monitoring the reduction of the absorbance at 570 nm vs. time (Fig. 4), we can see that it results faster for the low molecular weight compound **SP** and for both the terpolymers than for homopolymer poly[**SP**], Poly[**SP**-*co*-(*S*)-**AZ**] 1:1 having an intermediate trend.

However we have demonstrated that spiropyran moieties bonded to a macromolecular chain can isomerize as well as the corresponding low molecular weight compounds, if irradiated with light of suitable wavelength.

Furthermore, we have verified that copolymers containing optically-active azopyridine chromophores in the side chain, in the presence of TFA show significant changes in their electronic spectra similar to those ones displayed by the corresponding homopolymer poly[(*S*)-**AZ**] [17] (Fig. 5). In fact, the intensity of the band associated with electronic transitions of the azoaromatic chromophore at around 421 nm fades with a progressive growth of a new absorption band centred at 534 nm. The absence of well defined isosbestic points can plausibly be attributed to the presence of possible different monoprotonated species at the equilibrium, as previously discussed [17,36] and shown by NMR analysis [16].

The process is reversible and by adding an equal amount of a base (for example TEA), it is possible to restore the original spectra. These results suggest the possibility to obtain a two-state

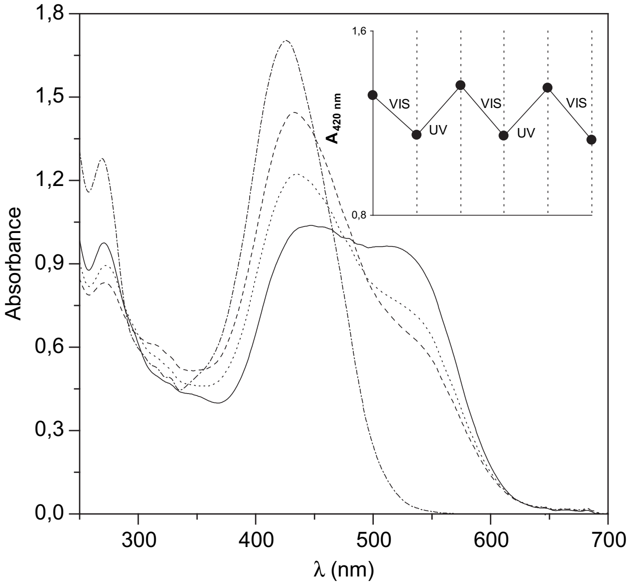


Fig. 5. Photochromic modulation of absorbance intensity of a solution of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 ($5\cdot10^{-4}$ M) in dichloroethane (-·-·-) in the presence of an equivalent of TFA before (—) and after (- - -) irradiation at 365 nm and after irradiation at 436 nm (···). Inset: relative intensity at 420 nm of the UV–vis spectra of the same solution measured after the first irradiation at 365 nm and after each subsequent irradiation step at either 436 (VIS) and 365 nm (UV).

molecular switch whose interconversion can be monitored by UV–VIS spectroscopy and envisage the opportunity to get a proton transfer between the azopyridine and the spiropyran dyes bonded to the same macromolecular chain.

4.3. Chiroptical properties

With the aim to study the optical activity of these materials and to reveal the presence of conformational dissymmetry, all the synthesized polymers have been investigated by CD spectroscopy in 1,2-dichloroethane solution, in the spectral region between 250 and 700 nm (Table 3 and Fig. 6).

As shown in Fig. 6, poly[**SP**-*co*-(*S*)-**AZ**] 1:1 displays a CD spectrum very similar to that one of the correspondent homopolymer poly[(*S*)-**AZ**] [17] exhibiting, in addition to a weak positive band around 270 nm related to the UV 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 (421 nm). Such a behaviour, typical of excitonic splitting, was previously reported for analogous 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 handedness. The sign of the exciton splitting, according to the chiral exciton coupling rules [38], suggests a left-handed screw sense of the coupled neighbouring azoaromatic chromophores.

Table 3
CD spectra of (*S*)-AZ and poly[(*S*)-AZ] polymers in dichloroethane solution at 25 °C.

Samples	1st band					2nd band	
	λ_1[a]	$\Delta\varepsilon_1$[b]	λ_0[c]	λ_2[a]	$\Delta\varepsilon_2$[b]	λ_3[a]	$\Delta\varepsilon_3$[b]
(*S*)-**AZ**[d]	420	+1.08	–	–	–	271	+0.26
Poly[(*S*)-**AZ**][d]	462	+6.71	425	400	−4.69	270	+0.22
poly[**SP**-*co*-(*S*)-**AZ**] 1:1	456	+3.88	421	401	−2.33	270	+0.34
Poly[(*S*)-**AZ**-*co*-**MMA**] 1:19	437	+0.72	–	–	–	271	+0.28
Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18	440	+0.80	–	–	–	276	+0.41
Poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8	436	+0.79	–	–	–	272	+0.56

[a] Wavelength (in nm) of maximum dichroic absorption.
[b] $\Delta\varepsilon$ expressed in $L\cdot mol^{-1}\cdot cm^{-1}$ and calculated for one repeating unit in the polymer.
[c] Wavelength (in nm) of the cross-over of dichroic bands.
[d] Ref. [17].

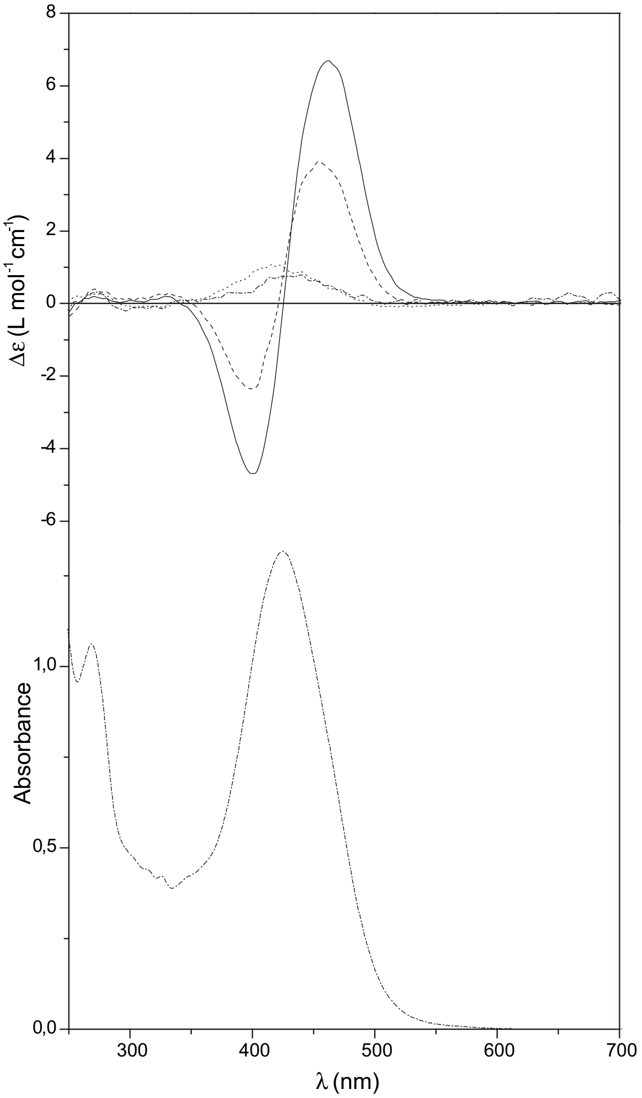


Fig. 6. (Bottom) UV–vis Spectra of poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 (-·-·) in dichloroethane solution. (Up) CD spectra of model (*S*)-**AZ** (···), poly[(*S*)-**AZ**] (—), poly[**SP**-*co*-(*S*)-**AZ**] 1:1 (- - -), and poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 (-·-·) in dichloroethane solution.

It is noteworthy that the excitonic couplet intensity decreases on passing from the homopolymer poly[(*S*)-**AZ**] to poly[**SP**-*co*-(*S*)-**AZ**] 1:1 (Table 3 and Fig. 6), confirming the reduction of interchromophoric interactions by insertion of spiropyran *co*-units, in agreement with UV–VIS spectroscopy. By the further addition of achiral methacrylic *co*-monomer (poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8 and 1:1:18), the excitonic couplet fades and CD spectra become more similar to the low molecular weight model (*S*)-**AZ**, displaying only two weak positive Cotton effects at 420 and 271 nm related to the first and second absorption bands of the azopyridine chromophore (Fig. 6), pointing out the absence of any structural restriction.

Further changes in the CD spectrum of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 can be induced throughout addition of TFA to the solution. As shown in

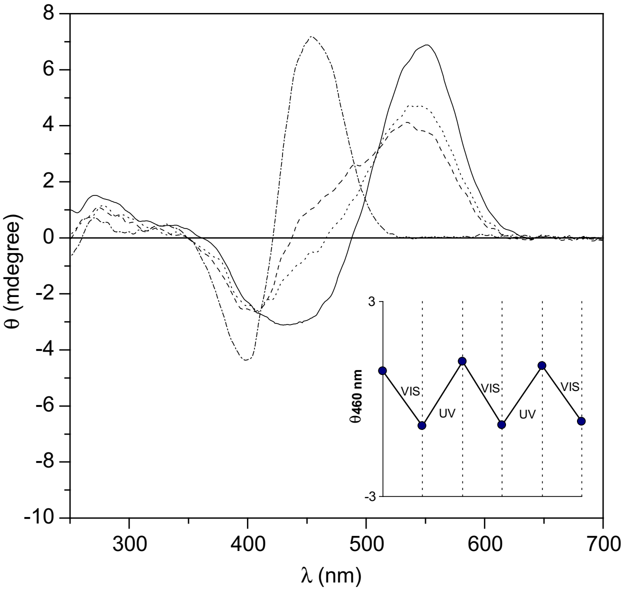


Fig. 7. Photochromic modulation of ellipticity intensity of a solution of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 in dichloroethane (5 × 10^{-4} M) (-·-·-) in the presence of an equivalent of TFA (—) under irradiation at 365 nm (···) and 436 nm (···). Inset: relative intensity at 460 nm of the CD spectra of the same solution measured after the first irradiation at 365 nm and after each subsequent irradiation step at either 436 (VIS) or 365 nm (UV).

Fig. 7, in fact, the excitonic couplet is preserved but it shows a strong bathochromic shift (cross-over point, $\Delta\epsilon = 0$, moving from 421 to 489 nm), consistently with UV–vis analysis, and an evident asymmetry, probably in consequence to the superimposition of two exciton splitting and/or CD bands having their maximum in correspondence to the UV maximum absorbance.

Anyway, the close similarity between the CD spectra of the polymeric solution before and after the addition of acid suggests that even if the protonation of azopyridine affects the dipolar interactions between side chain chromophores, the macromolecules maintain chiral conformations of one prevailing helical handedness at least for chain segments.

Furthermore, the reversibility of the protonation–deprotonation reaction only on the azopyridine chromophore (by adding an equal amount of a base such as triethylamine) seems to be promising for their application also as acid responsive organic materials based on chiroptical measurement [36].

Photoresponsive Properties and Photomodulation of Proton Transfer between Azopyridine and Spiropyran Dyes. In the literature, it is reported the possibility to photo-modulate proton transfer between low molecular weight spiropyran and azopyridine systems in solution [8,16]. Recently it was also demonstrated that the same process can take place between these functionalities bonded to distinct macromolecular chains [17]. Furthermore, the insertion of the chiral pyrrolidine group of one prevailing configuration between the polymeric backbone and the *trans*-azopyridine dye allows to monitor the obtained reversible and reproducible signal communication by CD as well as by UV–VIS spectroscopy.

In this context, the solutions of the investigated materials have been irradiated alternatively by UV and Visible light in the presence of an equivalent of TFA. All the derivatives displayed a behaviour similar to that one previously reported for the blend of the corresponding homopolymers [17].

As shown in Fig. 5 for copolymer poly[**SP**-*co*-(*S*)-**AZ**] 1:1, in fact, upon irradiation at 365 nm, the spiropyran moiety isomerizes to the open form which deprotonates (*S*)-**AZH** to give **MEH** and (*S*)-**AZ**. Such a behaviour is consistent with the absorption spectra changes: the absorption bands around 270 and 540 nm, related to **SP** and (*S*)-**AZH** respectively, decrease while that one at 425 nm, due to **MEH** and (*S*)-**AZ**, increases in intensity. The back isomerization of **MEH** to **SP** is obtained by irradiation at 436 nm, thus inducing proton-transfer to (*S*)-**AZ**. As a result, the absorption band related to merocyanine decreases while those one around 268 and 540 nm increase again.

However, the difference between the resulting absorption spectra upon irradiation at 436 nm and the original one, as shown in Fig. 5, suggests the composition of the photostationary state is different from that of the initial state. Nonetheless 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 420 nm, as shown in the inset of Fig. 5) with a good fatigue resistance.

For this type of applications, it is important to know the photostability resistance and which level of absolute signal will be stable for repeated cycles of irradiation.

All the investigated compounds show a similar trend (Fig. 8), but the average signal variation ΔA, expressed in absolute values as the variation of absorbance at 420 nm after subsequent UV–VIS irradiation, is more evident in polymeric materials (poly[**SP**-*co*-(*S*)-**AZ**] 1:1 ΔA = 0.19, homopolymer mixture ΔA = 0.21) than in the mixture of the corresponding monomers (ΔA = 0.12) and in the equimolar mixture of the two copolymers poly[**SP**-*co*-**MMA**] 1:19 and poly[(*S*)-**AZ**-*co*-**MMA**] 1:19 (ΔA = 0.11). Such a behaviour can be ascribed to the possibility of the polymers to reach a larger amount of merocyaninic form at the photostationary state, as discussed above, but it cannot be the only parameter affecting the process.

It is noteworthy, in fact, that poly[**SP**-*co*-(*S*)-**AZ**] 1:1 gives a signal communication very similar to the mixture of the two correspondent homopolymer (ΔA = 0.19 and 0.21, respectively), though they reach different amount of spiropyran opened form (**ME**) at the photostationary equilibrium, as revealed by the analysis reported above (15 and 30% respectively). These findings suggest that the proton transfer between spiropyran and azopyridine groups bonded to the same chain, is promoted, due to their closeness. Surprisingly, however, the best result in term of signal variation intensity (ΔA) is obtained for poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 (ΔA = 0.26) although it shows a ME% very similar to the monomeric compounds (ME% = 8) and even if the two chromophores are spaced out from

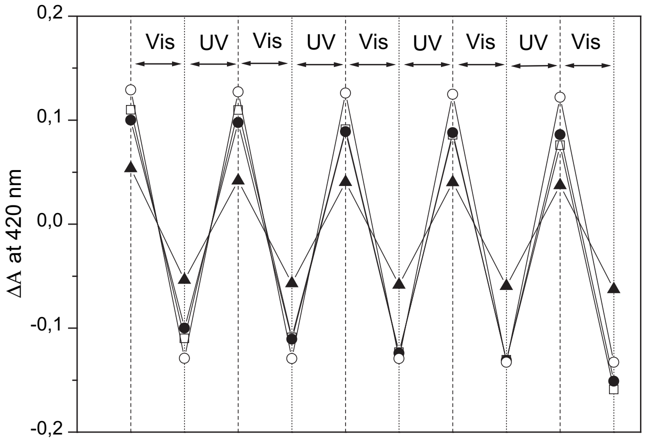


Fig. 8. Relative intensity at 420 nm of the UV–vis spectra of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 (●), poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 (○), a mixture of poly[SP] and poly[(*S*)-AZ] (□), and a mixture of poly[**SP**-*co*-**MMA**] 1:19 and poly[(*S*)-**AZ**-*co*-**MMA**] 1:19 (▲), in the presence of an equivalent of TFA, measured after the first irradiation at 365 nm and after each subsequent irradiation step at either 436 (VIS) or 365 nm (UV).

each other by the insertion of methacrylic *co*-units. It can be hypothesized that at this composition the conformational structure of the macromolecules minimizes repulsive interactions and allows the chromophores to stay close to each other thus promoting the proton transfer between them. Indeed, increased flexibility is displayed by poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 with respect to the copolymer poly[**SP**-*co*-(*S*)-**AZ**] 1:1, as suggested by the T_g values (Table 1).

The complete reversibility of the photoinduced variation of absorbance intensity of the investigated terpolymers and of the mixture of the two copolymers poly[**SP**-*co*-**MMA**] 1:19 and poly[(*S*)-**AZ**-*co*-**MMA**] 1:19, which is related to fatigue resistance properties, as shown in Fig. 8, allows to predict the possibility of application for these materials.

Indeed, after several irradiations steps with UV and Vis light alternatively acting on the same solution, the values of absorbance are quite similar. This indicates that no degradation photoreactions or relevant variation of the interchromophoric interaction take place. Thus, several cycles could be performed without any significant change in the proton-transfer behaviour.

Instead, the mixture of the two homopolymers and the copolymeric derivative having an equivalent (1:1) molar content of **SP** and (*S*)-**AZ** co-units also after few cycles of irradiation present a continue decrease of the values of absorbance related to the first UV–Vis absorption band (centred around 420 nm) (Fig. 8). This behaviour, similar to a “memory effect”, could be due to the aggregation of neighbouring azopyridine moieties or much in general to the irreversible variation of the dipolar interactions between neighbouring azoaromatic chromophores which are structurally favoured in the homopolymeric poly[(*S*)-**AZ**] and in the copolymer poly[(*S*)-**AZ**-*co*-**SP**] 1:1.

Again, the photoinduced changes in absorption spectra are accompanied by changes of dichroic signals. As reported in Fig. 7, CD spectra of poly[**SP**-*co*-(*S*)-**AZ**] 1:1 in presence of TFA, display an excitonic couplet at higher wavelength related to (*S*)-**AZH**. By irradiating this solution at 365 nm, as described above, the formation of the merocyanine system is promoted thus inducing a proton transfer from (*S*)-**AZH** to **ME**. Consistently, we can see a noticeable change in the position and shape of the dichroic bands related to the (*S*)-**AZ**/(*S*)-**AZH** ratio. The back isomerization is promoted by irradiation with Visible light and, as a result, the CD bands related to protonated (*S*)-**AZH** increase again. This phenomenon is reversible and the system does not show any degradation after several irradiation cycles (see inset in Fig. 7).

In summary, these studies show the possibility to tune the protonation of the azopyridinic group by controlling the photoisomerization of spiropyran bonded to the same macromolecular chain. The phenomenon can be monitored by UV–Vis spectroscopy as well as CD, and its reversibility and reproducibility, together with the good thermal stability of these materials, seem to be promising for applications in optical data storage or, more generally, in the field of photoresponsive systems.

5. Conclusions

New methacrylic copolymers, bearing in the side chain spiropyran moieties and the optically-active (*S*)-3-hydroxy pyrrolidinyl group linked through the nitrogen atom to an azopyridine chromophore, have been obtained by radical polymerization of the corresponding monomers.

The studies reported above demonstrate that the presence of the polymeric backbone does not prevent the chromophores to maintain their own properties. Furthermore, the presence of the chiral group of one single configuration interposed between the polymeric backbone and the *trans*-azopyridine chromophore provides these materials with the further possibility to assume a conformational dissymmetry of one prevailing screw sense, as revealed by the CD spectrum of poly[**SP**-*co*-(*S*)-**AZ**] 1:1. The presence of the excitonic couplet, in fact, even if reduced in amplitude with respect to the corresponding homopolymer poly[(*S*)-**AZ**], suggests that this macromolecule assumes chiral conformations of one prevailing helical handedness, at least for chain sections. It is noteworthy that by the further insertion of achiral methacrylic *co*-units (poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:8 and 1:1:18), CD spectra become more similar to that one of the low molecular weight (*S*)-**AZ**, pointing out the absence of any structural restriction.

Furthermore we have demonstrated the possibility to obtain a signal communication between spiropyran and azopyridine chromophores bonded to the same macromolecular chain, by irradiating the system with ultraviolet and/or visible light, and/or by pH variation. In the presence of acid, in fact, it is possible to modulate the protonation of the azopyridine group by photoisomerization of the spiropyran moiety. The obtained proton transfer can be monitored by UV–VIS spectroscopy as well as CD, and results completely reversible and reproducible. The obtained data reveal that the proton transfer is improved in poly[**SP**-*co*-(*S*)-**AZ**-*co*-**MMA**] 1:1:18 respect to the mixture of the corresponding monomers and homopolymers.

While poly[**SP**-*co*-(*S*)-**AZ**] 1:1 is characterized by strong dichroic effects, but lower stability to repeated cycles of irradiation, the terpolymer with a lower molar content of (*S*)-**AZ** and **SP** co-units (about 5%) displays an improved sensibility to proton-transfer process and, in addition, exhibits good stability to repeated cycles of irradiation with UV and Vis light.

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