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## Synthesis, characterization and photoconductive properties of optically active methacrylic polymers bearing side-chain 9-phenylcarbazole moieties

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#### ABSTRACT

The synthesis of two novel optically active monomers containing 9-phenylcarbazole moieties, such as (S)-(+)-2-methacryloyloxy-*N*-[4-(9-carbazolyl)phenyl]succinimide [(S)-(+)-**MCPS]** and (S)-(+)-3-metha cryloyloxy-*N*-[4-(9-carbazolyl)phenyl]pyrrolidine [(S)-(+)-**MCPP]**, is described. Each monomer has been radically homopolymerized to afford the corresponding optically active polymeric derivatives, which have been fully characterized. Their spectroscopic, thermal and photoconductive properties were compared to those of the new achiral homopolymer poly[*N*-(2-methacryloyloxyethyl)-*N*-[4-(9-carbazolyl)phenyl]ethylamine] {poly[**MCPE**]}, devised as an optically inactive macromolecular model compound, as well as to analogue polymeric derivatives containing side-chain optically active carbazolyl moieties. The chiroptical properties of the chiral polymers are quantitatively higher than in the corresponding monomers. Owing to the substantially stereoirregular structure of the main chain, this suggests that the overall optical activity is mainly due to conformational dissymmetry of the macromolecules. Spectroscopic evidence suggests the presence in all polymeric derivatives of dipole-dipole interactions between the 9-phenylcarbazolyl chromophores, occurring as a consequence of their anchorage to the polymer backbone, which favours their aggregation and justifies their high decomposition temperatures.

#### 1. Introduction

Carbazole has attracted considerable interest as building block in material science for its well known hole-transporting and electroluminescence properties [1].

Among various classes of photoconductive and photorefractive materials, carbazole-containing polymers are promising, since they possess outstanding and unique advantages over inorganic and organic crystals, such as the highest figure of merit, versatility in structural design, and good processability [2]. Such polymers have been used in advanced micro- and nanotechnologies as photoconductive and photorefractive media, in electroluminescent devices, as blue emitting materials and in holographic memories [3,4].

On the other hand, an intense interest has currently arisen into investigations concerning the amplification of chirality in polymeric materials, in solution as well as in the solid state [5–11],

because of their possible use in the general topic dealing with chiral nanotechnology [12,13].

Within this context, stereoregular helical polyacetylenes containing in the side chain the carbazole group functionalized with chiral minidendrons and with chiral menthyl, bornyl and triphenylamine groups [14–16] and optically active vinyl homo- and copolymers with side-chain carbazole moieties [17–20] have been reported.

To this regard, we have recently investigated the first example of optically active methacrylic polymers containing side-chain carbazole linked at their 3-position to the macromolecular main chain through an optically active group of one absolute configuration such as  $poly[(S)-(+)-2-methacryloyloxy-N-[3-(9-ethylcarbazole)]succinimide] {poly[(S)-(+)-$ **MECSI** $]} and poly-[(S)-(-)-3-methacryloyloxy-N-[3-(9-ethylcarbazole)]pyrrolidine] {poly[(S)-(-)-MECP]} [21].$ 

These materials are characterized, in solution, by chiral conformations related to the combined effects of the strongly dipolar conjugated carbazole system with the conformational stiffness of optically active rings, favouring the instauration of a conformational arrangement with a prevailing handedness, at least for chain sections of the macromolecules [21].

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Meanwhile, a wide range of vinyl monomers and their polymeric derivatives bearing various photo-active or electro-active chromophores have been extensively studied and applied in the field of advanced composites, optoelectronic materials and devices [22,23]. To this regard, polyacrylates and polymethacrylates with pendand 9-phenylcarbazolyl moiety have been largely studied in order to correlate the architecture of the chromophores to the photochemical and photophysical properties [24].

In the present study, in order to investigate how the macromolecular structure affects the hole transport mechanism and the photoconductive properties, we have envisaged the synthesis of polymeric derivatives bearing in the side chain a 9-phenylcarbazole moieties linked to the (*S*)-2-hydroxy-succinimide, or the (*S*)-3-hydroxy-pyrrolidinyl ring, as chiral moieties covalently linked to the main chain through ester bonds, such as poly[(*S*)-(+)-2-methacryloyloxy-*N*-[4-(9-carbazolyl)phenyl]succinimide] {poly[(*S*)-(+)-**MCPS**]} and poly[(*S*)-(+)-3-methacryloyloxy-*N*-[4-(9-carbazolyl)phenyl]pyrrolidine] {poly[(*S*)-(+)-**MCPP**]} (Fig. 1).

The presence of a strong electron-withdrawing or donating group such as the five membered cyclic succinimide moiety or the pyrrolidine residue, respectively, should induce highly conjugated system, potentially suitable to be used as photoconductive materials, electroluminescent devices, data storage, chemical photoreceptors, NLO, blue emitting materials and holographic memory.

Furthermore, the replacement of the alkyl substituent usually bound to the N atom of carbazole by a phenyl group, is also expected to expand the electronic conjugation in the molecules and to increase the glass transition temperature ( $T_g$ ) of these macromolecules.

Finally, the influence of chirality on the properties of the macromolecules was tested. This can be achieved by comparison with an analogous achiral polymeric derivative obtained by radical polymerization of the new monomer N-(2-methacryloyloxyethyl)-N-[4-(9-carbazolyl)phenyl]ethylamine [**MCPE**]. The structure of this polymeric model, poly[N-(2-methacryloyloxyethyl)-N-[4-(9-carbazolyl)phenyl]ethylamine] {poly[**MCPE**]} is reported in Fig. 1.

All the polymeric derivatives have been fully characterized and their spectroscopic properties compared to those of the corresponding monomers with the aim of evaluating the effect of the macromolecular structure on their physico-chemical properties. Photoconductivity measurements as a function of applied electric field under irradiation at fixed wavelength have been performed on the polymeric samples to investigate the effect of the presence of different electron-donating or withdrawing moieties linked to the carbazole group.

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Fig. 1. Chemical structures of the investigated polymers.

#### 2. Experimental section

#### 2.1. Materials and reagents

Methacryloyl chloride (Aldrich) was distilled (b.p.  $= 95 \,^{\circ}$ C) under dry nitrogen in the presence of traces of 2,6-di-*tert*.butyl-*p*-cresol as polymerization inhibitor just before use.

Triethylamine (TEA) (Aldrich) was refluxed over dry CaCl<sub>2</sub> for 8 h, then distilled (bp 89 °C). 2,2'-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use.

The optically active intermediate (S)-(+)-5-carboxymethyl-2-trichloromethyl-4-oxo-1,3-dioxolane (malic acid chloralide) was prepared starting from (S)-(-)-malic acid by reaction with chloral hydrate, according to literature procedures [25].

Toluene, chloroform, dichloromethane and tetrahydrofuran (THF) were purified and dried according to the reported procedures [26] and stored over molecular sieves (4 Å) under nitrogen.

Carbazole (Aldrich), *N*-ethyl-*N*-(2-hydroxyethyl)amine (Aldrich) and all other reagents and solvents (Aldrich) were used as received without further purification.

*N*-(4-aminophenyl)carbazole was prepared starting from crude carbazole with a synthetic procedure reported in literature [27].

(*S*)-(–)-3-Hydroxy-*N*-phenylpyrrolidine [(*S*)-(–)-**HPP**] [28] and 2-bromo-(*N*-ethylamine)ethanol [29] have been prepared as previously reported.

(*S*)-(–)-3-Hydroxy-*N*-(4-bromophenyl)pyrrolidine [(*S*)-(–)-**HPP**-**Br**] and 2-hydroxyethyl-*N*-ethyl-*N*-(4-bromophenyl)amine have been prepared as previously reported [30].

#### 2.2. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained at room temperature on 5– 10% CDCl<sub>3</sub> solutions using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm from tetramethylsilane (TMS) as the internal reference. <sup>1</sup>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. <sup>13</sup>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 sample prepared as KBr pellets.

Number average molecular weight  $(\overline{M}_n)$  and polydispersity  $(\overline{M}_w/\overline{M}_n)$  were determined in THF solution by SEC using an HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5  $\mu$  MXL column and a UV–Vis detector Linear Instruments model UVIS-200, working at 254 nm. Calibration curves were obtained by using several monodisperse polystyrene standards.

UV–Vis absorption spectra were recorded at 25 °C on a Perkin Elmer Lambda 19 spectrophotometer on CHCl<sub>3</sub> solutions by using cell path lengths of 1 and 0.1 cm for the 500–320 and 320–250 nm spectral regions, respectively. Carbazole chromophore concentrations of about  $5 \cdot 10^{-4}$  mol L<sup>-1</sup> were used.

Fluorescence spectra were recorded between 300 and 700 nm at  $25 \,^{\circ}$ C in 1 cm quartz cells with a Perkin Elmer LS55 spectro-fluorimeter.

Optical activity measurements were accomplished at 25 °C on CHCl<sub>3</sub> solutions with a Perkin Elmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 1 dm. Specific and molar rotation values at the sodium D line are expressed as deg dm<sup>-1</sup> g<sup>-1</sup> cm<sup>3</sup> and deg dm<sup>-1</sup> mol<sup>-1</sup> dL, respectively. Molar rotation for polymers refers to the molecular weight of the repeating unit.

Circular dichroism (CD) spectra were carried out at 25 °C on CHCl<sub>3</sub> solutions on a Jasco 810 A dichrograph, using the same path lengths and solution concentrations as for the UV–Vis measurements.  $\Delta \varepsilon$  values, expressed as L mol<sup>-1</sup> cm<sup>-1</sup> were calculated from the following expression:  $\Delta \varepsilon = [\Theta]/3300$ , where the molar ellipticity  $[\Theta]$  in deg cm<sup>2</sup> dmol<sup>-1</sup> refers to one carbazole chromophore.

The glass transition temperature ( $T_g$ ) values were determined by differential scanning calorimetry (DSC) on a TA Instrument DSC 2920 Modulated apparatus at a heating rate of 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 in air at a rate of 20 °C/min.

Samples for photoconductivity measurements were prepared by squeezing the material between two hot conductive (ITO) glasses, adjusting the thickness with glass spacers to 10 or 5  $\mu$ m. The cells were then quickly cooled to room temperature and the final real thickness measured by interferometry [31]. The samples containing diphenyl phthalate (DPP) (from Sigma–Aldrich, purified by recrystallization) as plasticizer, were prepared by first dissolving the components in chloroform and processing the resulting blend, after solvent evaporation, according to the method described above.

Photoconductivity data were obtained by applying a DC voltage to the sample and measuring the current with a Keithley 6517A Electrometer in the dark and under illumination. The illuminating light was provided by a Newport-Oriel 250 W Xenon lamp, coupled with a Newport-Oriel monochromator (mod 74,100), with a resulting light intensity I ~ 3 mW/cm<sup>2</sup> or, alternatively, by a laser light at 532 nm (from Laser Quantum, mod. Torus), with a light intensity I ~ 1 W/cm<sup>2</sup>.

#### 2.3. Synthesis of intermediate alcohols and monomers

## 2.3.1. (S)-(+)-2-Hydroxy-N-[4-(9-carbazolyl)phenyl]succinimide [(S)-(+)-**HCPS**]

Malic acid chloralide (9.9 g 0.0376 mol) was submitted to chlorination with excess of SOCl<sub>2</sub> (0.400 mol) to give, according to the reported procedure [25], the intermediate acid chloride which was directly submitted to the cyclization step. After evaporation under reduced pressure of any unreacted thionyl chloride, dry toluene (140 mL) and 9.7 g (0.0376 mol) of *N*-(4-aminophenyl)carbazole were added and the mixture heated at reflux under inert atmosphere for 12 h. The solvent was then evaporated under reduced pressure and the crude product purified by column chromatography (SiO<sub>2</sub>, eluent EtOAc/CH<sub>2</sub>Cl<sub>2</sub> 1:1 v/v) to give 5.6 g of pure (*S*)-(+)-**HCPS** (yield 52%).

 $[\alpha]_D^{25} = +5.9^\circ$  (*c* = 0.603 in CHCl<sub>3</sub>).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20–8.10 (d, 2H, arom. 2,7-H carbazole), 7.70– 7.65 (d, 2H, arom. 4,5-H carbazole), 7.60–7.55 (d, 2H, 15,19-H phenyl), 7.40 (m, 4H, arom. 1,3,6,8-H carbazole), 7.30 (m, 2H, 16,18-H phenyl), 4.85 (m, 1H, 2-CH), 3.40 (s, 1H, OH), 3.35 and 2.94 (2dd, 2H, 3-CH<sub>2</sub>) ppm.

FT-IR (KBr): 3458 ( $\nu_{OH}$ ), 3050 ( $\nu_{CH}$  arom.), 2967 ( $\nu_{CH}$  aliph.), 1706 ( $\nu_{C=0 \text{ imide}}$ ), 1600 ( $\nu_{C=C}$  arom.), 1514 ( $\delta_{CH}$ ), 1205 ( $\nu_{C-0}$ ), 850 and 830 ( $\delta_{CH}$  1,4-disubst. arom. ring), 744 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

#### 2.3.2. (S)-(+)-3-Hydroxy-N-[4-(9-carbazolyl)phenyl]pyrrolidine] [(S)-(+)-**HCPP**]

2.3.2.1. Method A. A 2 M solution of borane-dimethyl sulfide complex in THF (14.1 ml) was added dropwise, under inert atmosphere, to a stirred solution of (S)-(+)-**HCPS** (4 g, 0.00938 mol) in dry THF (45 ml) and the mixture kept under reflux for one night.

After evaporation of the solvent under reduced pressure, 4.8 g of sodium fluoride in dist. water (40 ml) were cautiously added to the solid residue, then the mixture was made acidic (pH 2) with conc. aq. HCl and refluxed 2 h. After treatment with 30% aq. NaOH (pH 10), the precipitated crude product was filtered and finally crystallized from hexane to afford 3.2 g of pure (*S*)-(+)-**HCPP** (yield 72%).

$$[\alpha]_D^{25} = +2.6^\circ$$
 (c = 0.542 in CHCl<sub>3</sub>).

2.3.2.2. Method B. A mixture of 7.12 g (0.024 mol) of carbazole, 0.55 g of *trans*-cyclohexanediamine (10% mol) and 0.46 g of airstable Cul (10% mol) was prepared in 15 ml of dry dioxane (1 M) in the presence of 7 g di K<sub>2</sub>CO<sub>3</sub> (2 equiv). Then, 6.92 g (0.029 mol) of (S)-(-)-3-hydroxy-N-(4-bromophenyl)pyrrolidine [(S)-(-)-**HPP-Br**] in dry dioxane (10 ml) were added and the resulting solution heated at reflux under inert atmosphere for 24 h. The cooled mixture was filtered-off and the organic solution washed with 0.1 M HCl, 5% Na<sub>2</sub>CO<sub>3</sub> and finally with water, in that order. After drying the organic phase over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporation of the solvent under reduced pressure, the crude reaction product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 1:1 v/v as eluent), followed by crystallization from abs. ethanol to give 6.8 g of pure product (yield 82.0%).

 $[\alpha]_D^{25} = +2.6^{\circ} \ (c = 0.525 \ in \ CHCl_3).$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.30–8.20 (d, 2H, arom. 2,7-H carbazole), 7.60– 7.35 (m, 8H, arom. 1,3,4,5,6,8-H carbazole and 15,19-H phenyl), 6.90 (d, 2H, 16,18-H phenyl), 4.90 (m, 1H, 3-CH), 3.60–3.50 (m, 4H, 2- and 5-CH<sub>2</sub>), 3.40 (s, 1H, OH), 2.40–2.20 (m, 2H, 4-CH<sub>2</sub>) ppm.

 $\begin{array}{l} FT-IR\,(KBr):\,3425\,(\nu_{OH}),\,3050\,(\nu_{CH}\,arom.),\,2967\,(\nu_{CH}\,aliph.),\,1605\\ (\nu_{C=C}\,arom.),\,1519\,(\delta_{CH}),\,1205\,(\delta_{C-0}),\,852\,\,and\,\,815\,(\delta_{CH}\,1,4-disubst.\,arom.\,ring),\,748\,(\delta_{CH}\,1,2-disubst.\,arom.\,ring)\,\,cm^{-1}. \end{array}$ 

## 2.3.3. N-(2-Hydroxy)-N-[4-(9-carbazolyl)phenyl]ethylamine [HCPE]

A mixture of 7.12 g (0.024 mol) of carbazole, 0.55 g of *trans*cyclohexanediamine (10% mol) and 0.46 g of air-stable CuI (10% mol) was prepared in 15 ml of dry dioxane (1 M) in the presence of 7 g di K<sub>2</sub>CO<sub>3</sub> (2 equiv). Then, 7.00 g (0.029 mol) of 2-hydroxyethyl-*N*-ethyl-*N*-(4-bromophenyl)amine in dry dioxane (10 ml) were added and the resulting solution heated at reflux under inert atmosphere for 24 h. The cooled mixture was filtered-off and the organic solution washed with 0.1 M HCl, 5% Na<sub>2</sub>CO<sub>3</sub> and finally with water, in that order. After drying the organic phase over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporation of the solvent under reduced pressure, the crude reaction product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 1:1 v/v as eluent) followed by crystallization from abs. ethanol to give 3.8 g of pure product (yield 48.0%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20 (d, 2H, arom. 2,7-H carbazole), 7.40–7.20 (m, 8H, arom. 1,3,4,5,6,8-H carbazole and 15,19-H phenyl), 6.90 (d, 2H, 16,18-H phenyl), 3.95 (d, 2H, N–CH<sub>2</sub>–C<u>H<sub>2</sub></u>), 3.50 (m, 4H, N–C<u>H<sub>2</sub></u>), 1.80 (m, 1H, OH), 1.20 (t, 3H, N–CH<sub>2</sub>–CH<sub>3</sub>) ppm.

 $\begin{array}{l} FT-IR \, (KBr): \, 3420 \, (\nu_{OH}), \, 3050 \, (\nu_{CH} \, arom.), \, 2967 \, (\nu_{CH} \, aliph.), \, 1605 \\ (\nu_{C=C} \, arom.), \, 1360 \, (\nu_{CHs} \, CH_3), \, 1231 (\nu_{C-O} \, alcohol), \, 847 \, and \, 816 \, (\delta_{CH} \, 1, \! 4\text{-disubst. arom. ring}) \, 746 \, (\delta_{CH} \, 1, \! 2\text{-disubst. arom. ring}) \, cm^{-1} \! . \end{array}$ 

## 2.3.4. (S)-(+)-2-methacryloyloxy-N-[4-(9-carbazolyl)phenyl]succi nimide [(S)-(+)-**MCPS**]

To an ice-cooled, vigorously stirred solution of (S)-(+)-**HCPS** (2 g, 0.0047 mol), triethylamine (0.79 ml, 0.0057 mol), dimethylamino pyridine (0.1 g) as catalyst, and 2,6-di-*tert*-butyl-4-methyl phenol (0.1 g) as polymerization inhibitor, in anhydrous THF (150 mL), methacryloyl chloride (0.79 ml, 0.0057 mol) in THF (5 ml) was added dropwise, under nitrogen atmosphere. The mixture was kept

ice-cooled for 2 h, then left at room temperature for one night, concentrated at reduced pressure and the crude product dissolved in chloroform. The chloroformic solution was washed with 0.1 M HCl, 5% Na<sub>2</sub>CO<sub>3</sub> and finally with water, in that order.

After drying the organic phase over anhydrous  $Na_2SO_4$  and evaporation of the solvent under reduced pressure, the crude reaction product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 4:1 v/v as eluent) followed by crystallization from abs. ethanol to give 1.70 g of pure product (yield 70.0%).

 $[\alpha]_D^{25} = +2.0^{\circ}(c = 0.996 \text{ in CHCl}_3).$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20–8.10 (d, 2H, arom. 2,7-H carbazole), 7.80– 7.70 (d, 2H, arom. 4,5-H carbazole), 7.60–7.55 (d, 2H, 15,19-H phenyl), 7.40 (m, 4H, arom. 1,3,6,8-H carbazole), 7.30 (m, 2H, 16,18-H phenyl), 6.35 and 5.75 (2dd, 2H, CH<sub>2</sub> methacrylic), 5.60 (m, 1H, 2-CH), 3.40 and 2.95 (d, 2H, 3-CH<sub>2</sub>), 2.00 (s, 3H, CH<sub>3</sub> methacrylic) ppm.

FT-IR (KBr): 3050 ( $\nu_{CH}$  arom.), 2967 ( $\nu_{CH}$  aliph.), 1716 ( $\nu_{C=0}$  ester), 1705 ( $\nu_{C=0}$  imide), 1633 ( $\nu_{C=C}$  methacrylic), 1600 ( $\nu_{C=C}$  arom.), 1512 ( $\delta_{CH2}$ ), 1460 ( $\nu_{CHas}$  CH<sub>3</sub>), 1356 ( $\nu_{CHs}$  CH<sub>3</sub>), 1230( $\delta_{C=0}$ ), 1161 ( $\nu_{C=0}$ ), 832 and 810 ( $\delta_{CH}$  1,4-disubst. arom. ring), 751 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

## 2.3.5. (S)-(+)-3-methacryloyloxy-N-[4-(9-carbazolyl)phenyl] pyrrolidine [(S)-(+)-**MCPP**]

The same procedure adopted for (*S*)-(+)-**MCPS** was followed starting from (*S*)-(+)-**HCPP** (3.5 g, 0.0107 mol), triethylamine (1.8 ml, 0.0128 mol), dimethylamino pyridine (0.2 g) and 2,6-di*tert*-butyl-4-methyl phenol (0.2 g) in THF (150 ml). The acylation reaction was performed by using methacryloyl chloride (1.24 ml, 0.0128 mol). Pure (*S*)-(+)-**MCPP** was obtained in 71.0% yield (2.25 g) by column chromatography purification (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 1:1 v/v as eluent) followed by crystallization from abs. ethanol.

$$[\alpha]_D^{25} = +9.3^{\circ}(c = 0.994 \text{ in CHCl}_3).$$

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20–8.10 (d, 2H, arom. 2,7-H carbazole), 7.40– 7.20 (m, 8H, arom. 1,3,4,5,6,8-H carbazole and 15,19-H phenyl), 6.80 (d, 2H, 16,18-H phenyl), 6.15 and 5.60 (2dd, 2H, CH<sub>2</sub> methacrylic), 5.55 (m, 1H, 3-CH), 3.60–3.40 (m, 4H, 2 and 5-CH<sub>2</sub>), 2.40–2.30 (m, 2H, 4-CH<sub>2</sub>), 1.95 (s, 3H, CH<sub>3</sub> methacrylic) ppm.

FT-IR (KBr): 3050 ( $\nu_{CH}$  arom.), 2967 ( $\nu_{CH}$  aliph.), 1718 ( $\nu_{C=0}$  ester), 1608 ( $\nu_{C=C}$  arom.), 1519 ( $\delta_{CH2}$ ), 1450 ( $\nu_{CHas}$  CH<sub>3</sub>), 1356 ( $\nu_{CHs}$  CH<sub>3</sub>), 1231 ( $\nu_{C-0}$  alcohol), 1161 ( $\nu_{C-0}$  ester) 850 and 815 ( $\delta_{CH}$  1,4-disubst. arom. ring), 748 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

## 2.3.6. N-(2-methacryloyloxyethyl)-N-[4-(9-carbazolyl)phenyl] ethylamine [MCPE]

The same procedure adopted for (*S*)-(+)-**MCPS** was followed starting from **HCPE** (3.3 g, 0.0097 mol), triethylamine (1.63 ml, 0.0128 mol), dimethylamino pyridine (0.2 g) and 2,6-di-*tert*-butyl-4-methyl phenol (0.2 g) in THF (100 ml). The acylation reaction was performed by using methacryloyl chloride (1.14 ml, 0.0117 mol). Pure **MCPE** was obtained in 55.0% yield (2.1 g) by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 1:1 v/v as eluent) followed by crystallization from abs. ethanol.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20 (d, 2H, arom. 2,7-H carbazole), 7.40–7.20 (m, 8H, arom. 1,3,4,5,6,8-H carbazole and 15,19-H phenyl), 6.90 (d, 2H, 16,18-H phenyl), 6.15 and 5.60 (d, 2H, CH<sub>2</sub> methacrylic), 4.50 (d, 2H, N–CH<sub>2</sub>–CH<sub>2</sub>), 3.70–3.50 (m, 4H, N–CH<sub>2</sub>), 2.00 (s, 3H, CH<sub>3</sub> methacrylic), 1.20 (t, 3H, N–CH<sub>2</sub>–CH<sub>3</sub>).

FT-IR (KBr): 3048 ( $\nu_{CH}$  arom.), 2978 ( $\nu_{CH}$  aliph.), 1716 ( $\nu_{C=0}$ ), 1623 ( $\nu_{C=C}$  methacrylic), 1605 ( $\nu_{C=C}$  arom.), 1520 ( $\delta_{CH2}$ ), 1450 ( $\nu_{CHas}$  CH<sub>3</sub>), 1371 ( $\nu_{CHs}$  CH<sub>3</sub>), 1169 ( $\nu_{C-0}$  ester), 852 and 814 ( $\delta_{CH}$  1,4-disubst. arom. ring), 753 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

#### 2.4. General polymerization procedure

The polymerization of the monomers was carried out in glass vials using AIBN as free radical initiator and THF as solvent. The reaction mixture (1.0 g of monomer, 2% weight of AIBN in 25 ml of THF) was introduced into the vial under nitrogen atmosphere, submitted to several freeze-thaw cycles and heated at 60 °C for 72 h. The reaction was then stopped by pouring the mixture into a large excess (200 ml) of methanol, and the coagulated polymer filtered-off. The solid polymeric product was repeatedly redissolved in THF at room temperature and reprecipitated again with methanol. The last traces of unreacted monomers and oligomeric impurities were eliminated by Soxhlet continuous extraction with methanol followed by acetone. The material was finally dried at 60 °C under vacuum for several days to constant weight.

Relevant data for the synthesized homopolymers are reported in Table 1.

#### 2.5. Spectroscopic data of polymers

#### 2.5.1. Poly[(S)-(+)-**MCPS**]

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20–7.80 (d, 2H, arom. 2,7-H carbazole), 7.80– 6.90 (m, 10H, arom. 1,3,4,5,6-H carbazole and 15,16,18,19-H phenyl.), 5.60 (m, 1H, 2-CH<sub>2</sub>), 3.40–2.95 (m, 2H, 3-CH<sub>2</sub>), 2.10–1.00 (m, 3H, CH<sub>3</sub> and CH<sub>2</sub> backbone) ppm.

FT-IR (KBr): 3050 ( $\nu_{CH}$  arom.), 2967 ( $\nu_{CH}$  aliph.), 1724 ( $\nu_{C=0}$  ester), 1600 ( $\nu_{C=C}$  arom.), 1512 ( $\delta_{CH2}$ ), 1365 ( $\nu_{CHs}$  CH<sub>3</sub>), 1200 ( $\nu_{C-0}$  ester), 850 and 834 ( $\delta_{CH}$  1,4-disubst. arom. ring), 748 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

$$[\alpha]_D^{25} = +6.4^\circ$$
 (c = 0.806 in CHCl<sub>3</sub>).

#### 2.5.2. Poly[(S)-(+)-MCPP]

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20–8.00 (d, 2H, arom. 2,7-H carbazole), 7.40– 7.00 (m, 8H, arom. 1,3,4,5,6,8-H carbazole and 15,19-H phenyl), 6.80–6.40 (m, 2H, 16,18-H phenyl), 5.40–5.00 (m, 1H, 3-CH), 3.70– 3.00 (m, 4H, 2- and 5-CH<sub>2</sub>), 2.40–0.80 (m, 7H, 4-CH<sub>2</sub> and backbone CH<sub>3</sub> and CH<sub>2</sub>) ppm.

FT-IR (KBr): 3050 ( $\nu_{CH}$  arom.), 2967 ( $\nu_{CH}$  aliph.), 1737 ( $\nu_{C=0}$  ester) 1608 ( $\nu_{C=C}$  arom.), 1519 ( $\nu_{CH2}$ ), 1451 ( $\nu_{CHas}$  CH<sub>3</sub>), 1365 ( $\nu_{CHs}$  CH<sub>3</sub>), 1161 ( $\nu_{C-0}$  ester), 851 and 814 ( $\delta_{CH}$  1,4-disubst. arom. ring), 746 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

$$[\alpha]_{D}^{25} = +9.0^{\circ}$$
 (c = 0.792 in CHCl<sub>3</sub>).

#### 2.5.3. Poly[MCPE]

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.20–8.00 (d, 2H, arom. 2,7-H carbazole), 7.40– 6.40 (m, 18H, arom. 1,3,4,5,6,8-H carbazole and 15,19-H phenyl), 6.80 (m, 2H, 16,18-H phenyl), 3.95 (m, 2H, N–CH<sub>2</sub>–C<u>H<sub>2</sub>)</u>, 3.70–3.50 (m, 4H, *N*-C<u>H<sub>2</sub></u>), 2.10–0.80 (m, 8H, N–CH<sub>2</sub>–C<u>H<sub>3</sub></u> and backbone CH<sub>2</sub> and CH<sub>3</sub>) ppm.

Table 1	
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Characterization data of	polymeric d	lerivatives
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Sample	Yield <sup>a</sup>	$\overline{M}_n^{\mathbf{b}}$	$\overline{M}_w/\overline{M}_n{}^b$	$T_{g}^{c}$	$T_d^d$
Poly[(S)-(+)- <b>MCPS</b> ]	83	11400	1.9	244	336
Poly[(S)-(+)-MCPP]	80	7000	1.9	194	343
Poly[MCPE]	80	10100	1.9	129	320

<sup>a</sup> Calculated as (g polymer/g monomer) 100.

<sup>b</sup> Determined by GPC in THF solution at 25 °C, expressed in g mol<sup>-1</sup>.

 $^{\rm c}$  Glass transition temperature determined by DSC at 10  $^{\circ}C/min$  heating rate under nitrogen flow, expressed in  $^{\circ}C.$ 

 $^{\rm d}$  Initial decomposition temperature as determined by TGA at 20 °C/min heating rate under air flow, expressed in °C.





FT-IR (KBr): 3048 ( $\nu_{CH}$  arom.), 2978 ( $\nu_{CH}$  aliph.), 1716 ( $\nu_{C=0}$  ester), 1605 ( $\nu_{C=C}$  arom.), 1520 ( $\nu_{CH2}$ ), 1450 ( $\nu_{CHas}$  CH<sub>3</sub>), 1371 ( $\nu_{CHs}$  CH<sub>3</sub>), 1169 ( $\nu_{C-0}$  ester.), 852 and 814 ( $\delta_{CH}$  1,4-disubst. arom. ring), 753 ( $\delta_{CH}$  1,2-disubst. arom. ring) cm<sup>-1</sup>.

#### 3. Results and discussion

#### 3.1. Synthesis of monomers

The synthesis of (S)-(+)-**MCPS** and (S)-(+)-**MCPP** was carried out according to Scheme 1, starting from the *N*-(4-aminophenyl)carbazole, obtained by Ullmann reaction [27] of carbazole with 1-bromo-4-nitrobenzene, followed by selective reduction to amine of the nitro group. The aromatic amine was submitted to reaction with the acyl chloride obtained by chlorination of (*S*)-malic acid chloralide, derived in turn from (*S*)-(-)-malic acid by reaction with chloral hydrate [25], to give the key intermediate (*S*)-(+)-2-hydroxy-*N*-[4-(9-carbazolyl)phenyl]succinimide [(*S*)-(+)-**HCPS**].

(S)-(+)-**HCPS** was then selectively reduced to the alcohol (S)-(+)-3-hydroxy-*N*-[4-(9-carbazolyl)phenyl]pyrrolidine [(*S*)-(+)-**HCPP**] with a synthetic procedure used for analogous chiral derivatives [28].

*N*-(2-hydroxy)-*N*-[4-(9-carbazolyl)phenyl]ethylamine **[HCPE**] (Scheme 1) was instead prepared starting from *N*-(4-bromophenyl)-*N*-ethyl-*N*-(2-hydroxyethyl)amine, derived in turn from the bromination of *N*-ethyl-*N*-(2-hydroxyethyl)phenylamine. This compound was coupled with carbazole, under Ullmann's conditions [27], to provide the desired alcohol.

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Sample	1st band 2nd		2nd band	2nd band 3rd band			4th band		5th band	
	$\lambda_{max}{}^{a}$	ε <sub>max</sub> b	$\lambda_{max}^{a}$	٤ <sub>max</sub> b	$\lambda_{max}^{a}$	ε <sub>max</sub> b	$\lambda_{max}{}^{a}$	٤ <sub>max</sub> b	$\lambda_{max}^{a}$	٤ <sub>max</sub> b
(S)-(+)- <b>MCPS</b>	-	-	283	14700	292	18600	325	3000	338	3200
Poly[(S)-(+)- <b>MCPS</b> ]	-	-	280	15500	293	19600	325	4500	339	3600
(S)-(+)- <b>MCPP</b>	268	25400	283	21500	292	20000	328	3200	341	3000
Poly(S)-(+)- <b>MCPP</b> ]	269	22800	283	20400	293	18900	329	4100	342	4600
MCPE	268	27900	283	24400	292	22150	326	3800	340	3400
Polv[MCPE]	269	22200	283	20100	293	18500	327	3900	341	3200

 Table 2

 UV-vis spectra in CHCl<sub>3</sub> solution at 25 °C of monomers and polymeric derivates.

<sup>a</sup> Wavelength of maximum absorbance, expressed in nm.

<sup>b</sup> Calculated for one single chromophore, expressed in Lmol<sup>-1</sup>cm<sup>-1</sup>.

The synthesis of (S)-(+)-**HCPP** was also carried out with the same synthetic procedure adopted for **HCPE** (Scheme 1) starting from the alcoholic intermediate (S)-(-)-3-hydroxy-*N*-phenyl-pyrrolidine [(S)-(-)-**HPP**], prepared as previously reported [28], giving essentially similar results as the above described synthetic method (see experimental part), with the aim to verify the occurrence of partial racemization in the course of the synthesis.

The three novel monomers (S)-(+)-2-methacryloyloxy-*N*-[4-(9-carbazolyl)phenyl]succinimide [(S)-(+)-**MCPS**], (S)-(+)-3-methacryloyloxy-*N*-[4-(9-carbazolyl)phenyl]pyrrolidine [(S)-(+)-**MCPP**] and *N*-(2-methacryloyloxyethyl)-*N*-[4-(9-carbazolyl)phenyl]ethylamine [**MCPE**] were finally obtained with good yields by esterification of the related alcohols with methacryloyl chloride.

The structures of all novel intermediates and final products were confirmed by <sup>1</sup>H NMR and FT-IR spectroscopy.

#### 3.2. Synthesis of polymers

The polymerization of the monomers, carried out in solution under free radical conditions by using AIBN as a thermal initiator, produced the corresponding polymeric derivatives in acceptable yields after purification, with average molecular weight and polydispersity values, as determined by gel permeation chromatography (GPC), in the range expected for this type of process. The polymeric products are completely soluble in common organic solvents such as CHCl<sub>3</sub> and THF, this feature favouring the possibility of their application as thin films.

Relevant data for the synthesized homopolymers are reported in Table 1.

The occurred polymerization was also proved by IR spectroscopy by checking the disappearance in the spectra of the absorption at 1630-1635 cm<sup>-1</sup>, related to the methacrylic double bond, and



**Fig. 2.** UV-vis spectra in CHCl<sub>3</sub> solution of poly[(S)-(+)-MCPP] (…) and poly[(S)-(+)-MCPS (—).

the contemporary appearance of the band at 1728–1731 cm<sup>-1</sup>, related to the carbonyl stretching vibration of the  $\alpha$ , $\beta$  saturated methacrylic ester group, shifted to higher frequency by ca. 10 cm<sup>-1</sup> with respect to the corresponding band of the monomeric precursors.

The <sup>1</sup>H NMR spectra of polymers, as compared to those of monomers (see experimental part), are also in agreement with the proposed structures. In accordance with FT-IR data, the resonances at 5.60 and 6.15 ppm, related to the methacrylic CH<sub>2</sub> protons, are absent in the <sup>1</sup>H NMR spectra of the polymers, and the methacrylic CH<sub>3</sub> resonance is shifted from 1.95 ppm to higher field. It is also to be noted that the resonances of the polymeric aromatic protons are shifted upfield to a variable extent with respect to the monomers, thus indicating the presence of shielding interactions between the side-chain chromophores in solution (see experimental part).

The microtacticity of synthesized polymers, as evaluated by integration of the  $^{13}$ C NMR signals related to the methacrylic methyl group at about 20 and 18 ppm, belonging to heterotactic *meso-racemo* (*mr*) and syndiotactic *racemo-racemo* (*rr*) triads [32], respectively, indicates a content of *rr* triads around 51–55%, with a probability of formation of *meso* and *racemo* dyads of 0.24–0.27 and 0.73–0.76, respectively, in agreement with literature reports concerning the radical polymerization of analogous methacrylic derivatives containing carbazole [21,33]. Thus, the main chain



**Fig. 3.** Fluorescence spectra of  $poly[(S)-(+)-MCPS](-\blacksquare-)$ , poly[(S)-(+)-MCPP](-), poly[MCPE](-),  $(S)-(+)-MCPS(-\Box-)$ ,  $(S)-(+)-MCPP(\cdots)$  and  $MCPE(\ldots)$  in CHCl<sub>3</sub>, excited at 293 nm (concentration about  $10^{-5}$  mol/L). The intensities are normalized to the concentration of carbazole unit.

#### Table 3

Specific and molar optical rotation data of the synthesized compounds in  $CHCl_3$  solution at 25  $^\circ C.$ 

Sample	$[\alpha]_D^{25a}$	$[\Phi]_D^{25\mathrm{b}}$
(S)-(+)- <b>MCPS</b>	+2.0	+8.5
Poly[(S)-(+)- <b>MCPS</b> ]	+6.4	+27.2
(S)-(+)- <b>MCPP</b>	+9.3	+38.2
Poly[( <i>S</i> )-(+)- <b>MCPP</b> ]	+9.0	+36.9

<sup>a</sup> Specific optical rotation, expressed in deg·dm<sup>-1</sup> g<sup>-1</sup>·dL.

<sup>b</sup> Molar optical rotation, calculated as  $([\alpha]_D^{25} \cdot M/100)$ , where *M* represents the molecular weight of the monomer or the molecular weight of the repeating unit of the polymer, in other word the molar optical rotation for carbazole unit, expressed in deg  $dm^{-1} \cdot mol^{-1} \cdot dL$ .

microstructure is essentially atactic, with a predominance of syndiotactic triads, suggesting a substantial low stereoregularity of the main chain.

#### 3.3. Thermal properties

The thermal stability of all polymeric derivatives, one of the most important features for the applicability of these materials, as determined by thermogravimetric analysis (TGA), resulted very high, with onset decomposition temperatures ( $T_d$ ) in the range 320–343 °C (Table 1), much higher than those reported for the classic polyvinylcarbazole (PVK) (227 °C) [34], deeply investigated as polymeric material for photorefractive applications [1], and other methacrylic carbazole-containing polymers [35] and is indicative of strong dipolar interactions in the solid state between the chromophores located in the macromolecular side chains. The highest  $T_d$  value (343 °C) displayed by poly[(S)-(+)-**MCPP**] can be thus attributed to increased inter- and/or intramolecular polar interactions between the neighbouring side-chain moieties.

As expected, only second-order transitions originated by glass transitions ( $T_g$ ), with no melting peaks, are observed in the DSC thermograms of the investigated polymers (Table 1), thus confirming that the macromolecules are substantially amorphous in the solid state. The high  $T_g$  values displayed by poly[(*S*)-(+)-**MCPS**] and poly[(*S*)-(+)-**MCPP**], as measured by DSC (224 and 194 °C, respectively) can be of interest for applications in optoelectronics and photonics (more stable photorefractivity, holographic storage, etc.); high values of  $T_g$  being in fact required in order to achieve enhanced temporal stability at room temperature of the electrically oriented dipoles in the bulk.

In particular, the  $T_g$  of poly[(*S*)-(+)-**MCPP**] is considerably higher, by about 65 °C, than that measured for poly[**MCPE**]. This behaviour is indicative of a reduced mobility of the macromolecular chains containing (*S*)-(+)-**MCPP** due to the presence of the conformationally rigid pyrrolidine ring interposed between the backbone and the 9-phenylcarbazole chromophore. Accordingly, poly[(*S*)-(+)-**MCPS**] containing the even more rigid succinimide ring, shows the highest  $T_g$  value. Again, in accordance with a reduced mobility of the macromolecular chains originated by their dipolar structure and conformational stiffness, the  $T_g$  values of the polymers investigated containing the residue of 9-phenylcarbazole are considerably higher than those of analogous polymers with aliphatic linear spacers between the carbazole chromophore and the methacrylic main chain [33,35–37].

The noticeable high thermal stability and  $T_g$  values suggest that these polymeric materials may be promisingly tested for commercial applications, besides the optical ones, where thermal stability is a fundamental requirement.

#### 3.4. UV-Vis and fluorescence properties

The UV–vis absorption spectra in CHCl<sub>3</sub> solution of monomers and polymers (Table 2 and Fig. 2) exhibit, in the region 250– 500 nm, evident absorption bands attributed to  $\pi$ - $\pi$ \* electronic transitions of the carbazole chromophore [38]. In accordance with Platt notation, these bands are related to three spectral regions, located between 350 and 315 nm ( ${}^{1}L_{b} \leftarrow {}^{1}A_{1}$  electronic transition), 310–280 nm ( ${}^{1}L_{a} \leftarrow {}^{1}A_{1}$  electronic transition) and 280–260 nm ( ${}^{1}B_{2} \leftarrow {}^{1}A_{1}$  electronic transition) [39].

The UV–vis absorption spectra of (*S*)-(+)-**MCPP** and poly[(*S*)-(+)-**MCPP**] display five absorption bands with maxima centered about at 268, 283 (shoulder), 292, 328 e 341 nm related to  $\pi$ – $\pi$ \* electronic transitions. By contrast, (*S*)-(+)-**MCPS** and poly[(*S*)-(+)-**MCPS**] show only four absorption bands of similar intensity centered at about 280 (shoulder), 293, 325 e 339 nm, related to the above mentioned electronic transitions of carbazole. The dissimilar nature of the bands can be ascribed to the presence of the succinimide residue, characterized by electron-withdrawing capability, originating lower electron density in the conjugated chromophoric system with respect to the pyrrolidine ring.

Achiral poly[**MCPE**] shows analogue absorptions bands as optically active poly[(S)-(+)-**MCPP**] (Table 2). This behaviour can be attributed to similar architectures of the phenylcarbazole moiety and electron-donating power of the amine nitrogen atoms located in the *N*-ethyloxy-*N*-ethylamine and pyrrolidine residues, respectively, which increase the electron density in the carbazole moiety.

In these last systems, while the maximum absorption wavelengths (Table 2) do not substantially change in going from the monomers to the related polymers, a remarkable hypochromic effect is observed when the spectra of (S)-(+)-**MCPP** and **MCPE**, where the lack of structural restraints originates a random distribution of the chromophores in dilute solution, are compared with those of the related polymers (Table 2).

This behaviour, frequently noticed in polymeric derivative bearing side-chain aromatic chromophores [19,30,33], is attributed to the presence of electrostatic dipole-dipole interactions between the neighbouring aromatic moieties [40–42] and confirms the occurrence of interactions between the side-chain carbazole groups (particularly in poly[**MCPE**]), which appear promising for achieving good photoconductivity even in the absence of dopants.

Fig. 3 shows the fluorescence spectra of synthesized polymers and relative monomers in CHCl<sub>3</sub> dilute solution (concentration of carbazole chromophore about  $10^{-5}$  mol/L) excited at 293 nm.

#### Table 4

CD spectra in CHCl <sub>3</sub> solution at 25	°C of monomers and	polymeric derivatives
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Sample	1st band		2nd band	d	3rd band	1	4th band	l	5th band	
	$\lambda_1^a$	$\Delta \varepsilon_1{}^{\mathbf{b}}$	$\lambda_2^a$	$\Delta \varepsilon_2^{\mathbf{b}}$	$\lambda_3^a$	$\Delta \varepsilon_3^{\mathbf{b}}$	$\lambda_4^a$	$\Delta \epsilon_4{}^{\rm b}$	$\lambda_5^a$	$\Delta \varepsilon_5^{\mathbf{b}}$
(S)-(+)- <b>MCPS</b>	266	+0.42	286	+0.94	-	_	-	-	338	+0.21
Poly[(S)-(+)- <b>MCPS</b> ]	268	+0.81	278	+0.70	308	+2.21	-	-	342	+0.40
(S)-(+)- <b>MCPP</b>	269	-0.24	290	+0.56	-	-	324	+0.23	-	-
Poly[(S)-(+)- <b>MCPP</b> ]	269	-1.56	288	+0.57	-	-	334	+0.25	347	+0.23

<sup>a</sup> Wavelength of maximum dichroic absorption, expressed in nm.

<sup>b</sup> Calculated for one repeating unit in the polymer, expressed in Lmol<sup>-1</sup>cm<sup>-1</sup>.



**Fig. 4.** CD spectra in CHCl<sub>3</sub> solution of (S)-(+)-**MCPP**(---) and poly[(S)-(+)-**MCPP**](-).

Both the solutions of (S)-(+)-**MCPP** and **MCPE** emit strong fluorescence in the blue region with maximum wavelength at about 407 and 408 nm, respectively. Poly[(*S*)-(+)-**MCPP**] and poly[**MCPE**] emit in a similar manner, with a small intensity quenching with respect to the related monomers. This similar fluorescence spectroscopic pattern suggests that the 9-phenylcarbazole moieties in the side-chain emit regardless the presence of the polymethacrylate backbone, at least in dilute solution, and the different electron-donating properties of amine and pyrrolidine nitrogen atoms.

The fluorescence spectra of (S)-(+)-**MCPS** and poly[(*S*)-(+)-**MCPS**] show two strong emission bands at  $\lambda_{max}$  values of about 348 and 362 nm, with a shoulder at about 383 nm which should be due to fluorescence of the carbazole chromophore (Fig. 3). Clearly, the fluorescence efficiency is significantly lower for the polymeric sample (quenching) than for the monomer. This behaviour is due to the existence of intramolecular interactions between neighbouring carbazole chromophores along the polymer chains [24].

The above results clearly demonstrate that the strength and the type of the inter- and intrachromophoric interactions in carbazolecontaining polymers can be tuned by the electron-withdrawing and donating properties of the substituent at carbazole so as to give rise to different photoconductive mechanisms.

#### 3.5. Chiroptical properties

The dependence of optical activity on the macromolecular structure was assessed by measuring the specific  $\{[\alpha]_D^{25}\}$  and molar  $\{[\Phi]_D^{25}\}$  optical rotation in chloroform solution at the sodium D line of monomers and related polymers (Table 3).

Poly[(*S*)-(+)-**MCPS**] shows higher specific and molar optical rotation values than the corresponding monomer, thus suggesting a conformational contribution to the overall optical activity by the macromolecules with respect to (*S*)-(+)-**MCPS**. Instead, poly[(*S*)-(+)-**MCPP**] and (*S*)-(+)-**MCPP** display substantially similar optical activity.

To investigate in more detail their chiroptical properties, monomers and polymers have been submitted to CD spectroscopy in chloroform solution in the spectral region between 250 and 650 nm (Table 4, Figs. 4 and 5).

The CD spectra of poly[(S)-(+)-MCPS] and poly[(S)-(+)-MCPP] are characterized by dichroic signals in correspondence to the UV– Vis absorption bands. These signals, which are related to the electronic transitions of the 9-phenylcarbazolyl chromophores, are more intense than those measured on the corresponding monomers. The imperfect correspondence of the bands between the CD and UV–vis spectrum can be explained by considering that they are originated by a sum of electronic transitions which can be differently influenced by the chirality of the macromolecules.

In particular, the CD spectra of poly[(S)-(+)-MCPP] and (S)-(+)-MCPP exhibit four and three dichroic bands, respectively (Fig. 4 and Table 4). The monomer shows one negative signal at 269 nm and two positive signals at 290 and 324 nm of low intensity, while the polymer shows more intense signals at the same wavelengths (particularly relevant the negative dichroic absorption around 269 nm) and one additional positive dichroic band around 347 nm with respect to the monomer.

The CD spectrum of poly[(*S*)-(+)-**MCPS**] exhibits four relevant positive dichroic bands ( $\lambda_{max} = 342$ , 308, 278 and 268 nm) in the spectral region related to the  $\pi$ - $\pi^*$  electronic transition of the carbazole chromophore (Table 4). Significantly, the CD spectrum of the corresponding monomer (*S*)-(+)-**MCPS** displays only three weak positive dichroic signals ( $\lambda_{max} = 338$ , 286 and 266 nm), related to its UV–vis absorptions (Fig. 5 and Table 4).

It appears, therefore, that the presence of an optically active cyclic residue of one prevailing absolute configuration, interposed between the main chain and the 9-phenylcarbazole residue, favours to some extent the establishment of conformational dissymmetry in the macromolecules and chiral perturbation on the electronic transitions of the 9-phenylcarbazole chromophore [30]. These effects, previously observed in several polymers bearing optically active side-chain carbazole [21] or azocarbazole [30.33] chromophores arranged in a mutual chiral geometry of one prevailing handedness, at least for chain segments of the macromolecules in solution [9,43-45], should be due to the presence of dipole-dipole interactions between neighbouring carbazole groups, as suggested by the UV-vis spectra in solution. Indeed, similar dipolar interactions are absent in the spectrum of monomers, that do not have any structural restriction in dilute solution and thus are unable to produce cooperative chiral interactions between the chromophores.

The CD spectra of poly[(*S*)-(+)-**MCPS**] and poly[(*S*)-(+)-**MCPP**] registered in the temperature range  $10-40 \degree C$  at concentrations of carbazole repeating unit varying within  $10^{-6}-10^{-2} \mod L^{-1}$ ,



**Fig. 5.** CD spectra in CHCl<sub>3</sub> solution of (*S*)-(+)-**MCPS** (---) and poly[(*S*)-(+)-**MCPS**] (—).



**Fig. 6.** Photoconductivity vs. the electric field at 532 nm of poly[**MCPE**] mixed with 15% w/w of DPP ( $\blacktriangle$ ), pure poly[(*S*)-(+)-**MCPP**] ( $\triangle$ ) and poly[(*S*)-(+)-**MCPS**] mixed with 15% w/w of DPP ( $\blacklozenge$ ). Inset: enlargement of pure poly[(*S*)-(+)-**MCPP**] ( $\triangle$ ) and poly[(*S*)-(+)-**MCPS**] with 15% w/w of DPP ( $\blacklozenge$ ).

resulted, in the limit of experimental errors, practically unchanged. This confirms the presence of intramolecular interactions between side-chain chromophores which appear stable at least in the range of temperatures investigated.

However, the contribution by conformational dissymmetry to the overall optical activity of the synthesized polymers appears of limited extent with respect to the previously investigated [21] poly[(*S*)-(+)-**MECSI**] ({[ $\Phi$ ]<sub>D</sub><sup>25</sup>} = +668.0) and poly[(*S*)-(-)-**MECP**] ({[ $\Phi$ ]<sub>D</sub><sup>25</sup>} = +200.7), as suggested also by the specific optical rotatory power at the sodium D line. In fact, the homopolymers bearing the 9-phenylcarbazolyl group linked to the nitrogen atom of the pyrrolidine or succinimide ring through the phenyl substituent display [ $\Phi$ ]<sub>D</sub><sup>25</sup> values about one order of magnitude lower than the derivatives having the chiral succinimide and pyrrolidine residues directly linked to the carbazole chromophore, thus indicating that in the latter a much more efficient chirality induction on the carbazole moiety takes place.

#### 3.6. Photoconductive properties

All the polymeric samples, given the presence of the carbazole moiety which is well known for its hole conducting properties [1], do not require the addition of dopants in order to exhibit photo-conductivity. The main results obtained are shown in Fig. 6 and Table 5.

As reported in the inset of Fig. 6, pure poly[(*S*)-(+)-**MCPP**] shows higher photoconductivity than poly[(*S*)-(+)-**MCPS**] (85 wt % + 15 wt % DPP). This different behaviour cannot be ascribed to the presence of the plasticizer DPP and to the absorption coefficients of the materials at  $\lambda$  = 532 nm, that appear quite similar,  $\alpha$  = 147 cm<sup>-1</sup>

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Photoconductivity of the investigated polymers.

Sample (% DPP) <sup>a</sup>	$\sigma/I^{b}$	σ/I <sup>c</sup>	$\alpha^{\mathbf{d}}$	$\sigma/\alpha I^e$
Poly[( <i>S</i> )-(+)- <b>MCPS</b> ] (15%) Poly[( <i>S</i> )-(+)- <b>MCPP</b> ] Poly[ <b>MCPE</b> ] (15%)	$3.5 \times 10^{-13}$ $7.8 \times 10^{-13}$ $1.3 \times 10^{-11}$	$\begin{array}{c} 8.3{\times}10^{-13}\\ 1.6{\times}10^{-12}\\ 2.4{\times}10^{-11}\end{array}$	118 147 78	$\begin{array}{c} 7.0 \times 10^{-15} \\ 1.1 \times 10^{-14} \\ 3.1 \times 10^{-13} \end{array}$

<sup>a</sup> Weight % of plasticizer (DPP) in the sample.

<sup>b</sup> Photoconductivity expressed in  $\sigma/I$  (S cm W<sup>-1</sup>) at 18 V/ $\mu$ m.

<sup>c</sup> Photoconductivity expressed in  $\sigma/I$  (S cm W<sup>-1</sup>) at 35 V/ $\mu$ m.

<sup>d</sup> Absorption coefficient at 532 nm expressed in cm<sup>-1</sup>

 $^{e}~$  Photoconductivity expressed in  $\sigma/\alpha I~(S~cm^{2}~W^{-1})$  at 35 V/µm.

for poly[(*S*)-(+)-**MCPP**] and  $\alpha = 118 \text{ cm}^{-1}$  for poly[(*S*)-(+)-**MCPS**] (85 wt % + 15 wt % DPP). The difference between the samples has therefore to be more likely attributed to the presence of a charge-transfer (CT) complex [24] between the strong electron donator pyrrolidine and carbazole in poly[(*S*)-(+)-**MCPP**], as evidenced by the emission band at 407 nm in the fluorescence spectrum. In fact, CT process can positively affect photoconductivity by two different mechanisms: photogeneration efficiency, due to the stabilization of charged species, and transport parameters, which can be favoured by more efficient holes hopping between more electron-rich carbazole moieties.

By contrast, poly[MCPE] (85 wt % + 15 wt % DPP) (Fig. 6 and Table 5) shows a considerable higher value of photoconductivity with respect to poly[(S)-(+)-MCPS] and the analogous poly[(S)-(+)-MCPP]. This behaviour can be ascribed to the different structure of the repeating units: in poly[MCPE], the 9-phenylcarbazole residue is linked to the backbone through a flexible spacer, whereas in (S)-(+)-MCPS and (S)-(+)-MCPP units, the conformational freedom of the carbazole chromophore is limited by the five membered succinimide and pyrrolidine rings, so as to reduce the mobility of the side chains. These results suggest that the appropriate flexibility of the spacer connecting the carbazole moiety to the main chain may favour the adoption of a convenient mutual geometry of the neighbouring 9-phenylcarbazole chromophores, thus allowing a better carrier transport via hopping process with consequent improvement of the photoconductive properties of the material.

#### 4. Conclusions

Novel chiral homopolymeric methacrylates, poly[(S)-(+)-MCPS] and poly[(S)-(+)-MCPP] have been obtained by radical polymerization of the related novel monomers, bearing the optically active residues of (S)-2-hydroxy-succinimide and (S)-3-hydroxy-pyrrolidine, respectively, interposed between the main chain and the 9-phenylcarbazole chromophore.

In order to evaluate the influence of the chirality on the properties of these macromolecules, an analogous achiral new polymer {poly[**MCPE**]} has been also synthesized.

The presence of strong dipolar interactions between the sidechain 9-phenylcarbazole groups in the solid state also produces relevant thermal properties with high values of  $T_g$  and  $T_d$  which can be of interest for nanoscale technological applications.

Absorption and fluorescence spectra confirm the presence of dipolar interaction between neighbouring 9-phenylcarbazole moieties.

The optical activity shown by the chiral homopolymers with respect to the related monomers indicates that the macromolecules assume, in solution, conformations with a prevailing chirality, at least for chain sections of the macromolecules, as demonstrated by the presence in the CD spectra of dichroic signals, related to the electronic transitions of the 9-phenylcarbazole chromophores. However this effect is remarkably reduced with respect to previously investigated analogous polymeric derivatives bearing the chiral moiety directly linked to the carbazole group.

The photoconductivity measurements indicate that the presence of a flexible spacer interposed between the main chain and the 9-phenylcarbazole chromophore favours the adoption of chromophore conformations suitable to provide a better carrier transport via hopping process.

The properties of this class of optically active carbazole polymers, bearing at the same time different chemical functionalities, may allow a variety of potential applications based on photoconductive properties.

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