

# Chiroptical and optical thermoplastic acid sensors based on chiral methacrylic polymers containing azoaromatic moieties

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## Abstract

We present here a preliminary report on the interaction between a new class of chiral azo-polymers with protic acids. The experiments have been carried out on amorphous thin films obtained by spin coating. The investigated polymers display reversible changes of their UV–vis spectra and chiroptical properties (evidenced by circular dichroism measurements) in response to external chemical stimuli, thus suggesting their potential use as ultrathin thermoplastic sensors.

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## 1. Introduction

Azo dyes represent one relevant class of commercial organic colorants [1,2], as evidenced by the wide number of studies on their physico-chemical properties, which include also pharmaceuticals [3,4], sensors [5–8] and technologically advanced applications [9–12]. As a consequence, extensive research has been carried on, and is still in progress, into the fields of application of these materials. In particular, it is well known that azo dyes may undergo protonation, with a consequent strong variation of their physico-chemical properties, especially the electronic ones [13–15].

On the other hand, the induction of chirality of helical in polymers has attracted widespread interest because of its possible applications in optical devices or data storage and also because of its relevance to chiral amplification as it may have occurred at the early stages of life [16].

Recently [17,18], we have synthesized and investigated methacrylic polymers bearing in the side chain the chiral cyclic (*S*)-3-hydroxypyrrolidine moiety interposed between the main chain and the *trans*-azoaromatic chromophore, substituted or not in the 4' position by an electron-withdrawing group, such

as (poly[(*S*)-3-methacryloyloxy-1-(4-azobenzene)pyrrolidine] {poly[(*S*)-MAP]} [17] and poly[(*S*)-3-methacryloyloxy-1-(4'-cyano-4-azobenzene)pyrrolidine] {poly[(*S*)-MAP-C]} [18] (Fig. 1). In these materials, the presence of a rigid chiral moiety of one prevailing absolute configuration favours the establishment, both in solution and in the solid state as thin films, of a chiral conformation of one prevailing helical handedness at least within chain segments of the macromolecules, which can be observed by circular dichroism (CD) spectroscopy.

The presence of both the azoaromatic and chiral functionalities allows the polymers to display both the properties typical of dissymmetric systems (optical activity, exciton splitting of dichroic absorptions), as well as the features typical of photochromic materials (photorefractivity, NLO properties) [19–22] which may open the way to their use as chirality-sensitive photoresponsive materials.

In this context, we present here a preliminary report on the interaction between this new class of chiral azo-polymers with protic acids. The experiments have been carried out in solution and in the solid state on amorphous thin films obtained by spin coating.

## 2. Experimental

UV–vis absorption spectra were recorded at 25 °C in the 700–250 nm spectral region with a Perkin-Elmer Lambda 19

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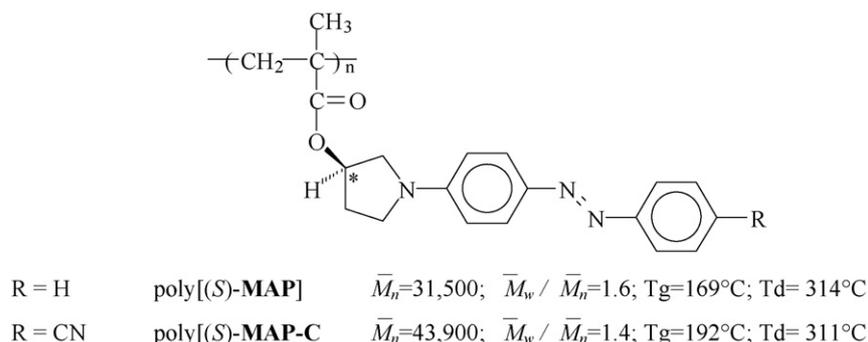


Fig. 1. Chemical structures and characterization data of the studied polymers.

spectrophotometer on  $\text{CHCl}_3$  solutions by using cell path lengths of 1 cm. Concentrations in azoaromatic chromophores of about  $3 \times 10^{-5} \text{ mol L}^{-1}$  were used. Circular dichroism spectra were carried out at 25 °C on a Jasco 810 A dichrograph, using the same path lengths, solutions and concentrations as for UV–vis measurements.  $\Delta\epsilon$  values, expressed as  $\text{L mol}^{-1} \text{ cm}^{-1}$  were calculated from the following equation:  $\Delta\epsilon = [\Theta]/3300$ , where the molar ellipticity  $[\Theta]$  in  $\text{deg cm}^2 \text{ dmol}^{-1}$  refers to one azoaromatic chromophore. Amorphous thin films of poly[(S)-MAP] and poly[(S)-MAP-C] have been prepared by spin coating of a solution of the polymer in 1-methyl-2-pyrrolidinone/tetrahydrofuran (NMP/THF) onto clean fused silica (or glass slides). The films were then dried by heating above 80 °C under vacuum for 12 h. The films thickness, measured by a Tencor P-10 profilometer, was in the range 150–350 nm. The films were submitted to exposure to HCl and subsequently  $\text{NH}_3$  vapours at room temperature for few seconds to completely visible colour change and their CD and UV–vis spectra carried out under the same instrumental conditions as the related solutions.

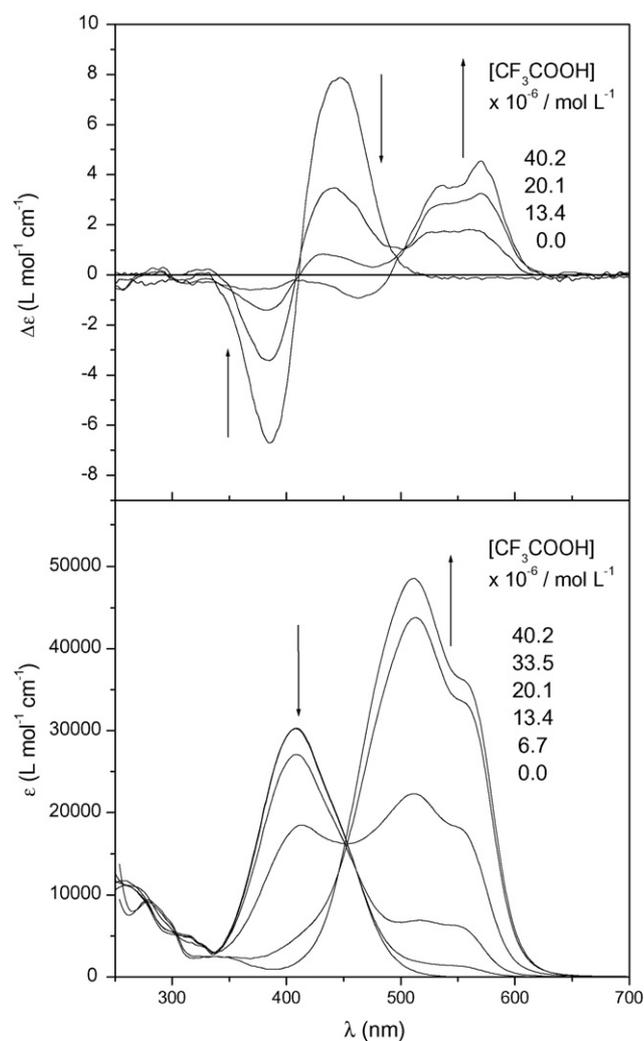
### 3. Results and discussion

#### 3.1. UV–vis and chiroptical properties in solution

The presence of increasing concentrations of  $\text{CF}_3\text{COOH}$  (up to  $40.2 \times 10^{-6} \text{ mol L}^{-1}$ ) in  $3 \times 10^{-5}$  molar  $\text{CHCl}_3$  solutions of the polymeric derivatives poly[(S)-MAP] and poly[(S)-MAP-C] affords a significant change of their electronic spectra.

As shown in Fig. 2 for poly[(S)-MAP], it can be noticed that the intensity of the band due to the combined contributions of the  $n-\pi^*$ , first  $\pi-\pi^*$  and intramolecular charge-transfer electronic transitions of the azobenzene chromophore [23], centred at about 408 nm, decreases with a progressive growth of two new signals centred at 510 and 560 nm. In addition to the new bands, three isosbestic points are evident at around 305, 340 and 450 nm throughout the reaction, pointing out the presence of two different absorbing species in solution [24]. The protonation of poly[(S)-MAP-C] in solution occurs in a similar stepwise manner. The observed new absorption bands can be plausibly attributed to the different monoprotonated species reported in Scheme 1, as suggested by comparison of their wavelength

with those of analogous low molecular weight azoaromatic chromophores previously investigated [14,15,25–28]. For example, the monoprotection of 4-(dimethylamino)azobenzene with HCl in ethanolic solution results in a decrease of intensity of the original band at about 400 nm with a progressive growth of a new signal at 516 nm [27]. This new long-wavelength

Fig. 2. Change of CD (up) and UV–vis (down) spectra in  $\text{CHCl}_3$  solution at 25 °C of poly[(S)-MAP] ( $3.40 \times 10^{-5} \text{ mol L}^{-1}$ ) upon addition of  $\text{CF}_3\text{COOH}$ .

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