OPTICAL PROPERTIES OF POLYSTYRENE DOPED WITH *P*-NITROANILINE DERIVATIVES

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New copolymers of styrene with N-acryloyl p-nitroaniline or N-diethyl methylenemalonate p-nitroaniline chromophores were synthesized and characterized by size exclusion chromatography (SEC), thermal analyses (DSC, TGA) and reflectometry. The linear optical properties of the polystyrene copolymers and the polystyrene (PS) doped with p-nitroaniline derivative chromophores were investigated and were related to the chromophore content in the matrix by prism coupling at 633 nm. Thin films of the polymers with good optical quality were prepared by the spin coating method. The glass transition and decomposition temperatures and the refractive index profile of the copolymers were similar to those of the parent PS. On the other hand, the PS doped with p-nitroaniline derivative chromophores had lower glass transition temperatures attributed to the plasticizing effect of the chromophore and different refractive index profiles compared with the parent PS.

Keywords: *Polystyrene, p-nitroaniline derivative, spin coating, refractive index, waveguide.*

1. Introduction

Polymers have been extensively studied as promising materials for integrated optical devices due to the broad spectrum of possible applications in data transmission and processing systems [1-4]. The refractive index profile is the most important characteristic in a waveguide cross-section and defines the properties of the optical waveguide as an informational system element and thus determines the performance of the whole planar device [5-7]. Polymers have become, in the last few decades, very attractive for photonic devices because they are easily processed, offer high flexibility and tailor-made properties and have a relatively low cost.

Investigations focused on conventional linear polymers, such as polymethylmethacrylate (PMMA), polystyrene or polycarbonate, have demonstrated the great potential for their use as waveguides at relatively short wavelengths [8-10]. The modification of the properties of these polymers by adding chromophores [11, 12] into the polymer or attaching them to the backbone has attracted considerable interest [13]. Several types of chromophores with functional groups in a particular direction of orientation have been investigated in order to control the polymer properties. The *p*-nitroaniline derivative chromophores [14] are well known conjugated π-electron systems, with electron donor and acceptor groups attached to

opposites sides of the molecule which induce an intramolecular charge transfer and consequently enhance the refractive index and first order hyperpolarizability β [15,16].

In this study, new copolymers of styrene with N-acryloyl *p*-nitroaniline or N-diethyl methylenemalonate *p*-nitroaniline chromophores were synthesized and their thermal and optical properties were evaluated. Also, polystyrene doped with *p*-nitroaniline derivatives was assessed for application as a waveguide. The refractive index profile of thin polymeric films produced by the spin coating method was evaluated.

2. Experimental

2.1. Materials

Polymerization-grade styrene supplied by INNOVA S.A. (Brazil) was used as received. The *p*-nitroaniline derivative chromophores N-acryloyl *p*-nitroaniline or N-diethyl methylenemalonate *p*-nitroaniline, named here *p*-NA acryloyl and *p*-NA malonate, respectively, used as comonomers, were synthesized according to the literature [17]. 2,2'– Azobisisobutyronitrile (AIBN) used as the polymerization initiator was recrystallized from methanol. All solvents for the copolymer synthesis and characterization were used as received.

2.2. Polymer synthesis

In a sealable 5 mL tube, 3.12 g (30 mmol) of styrene, and 14.4 mg (0.075 mmol) of *p*-NA acryloyl or 23.1 mg (0.075 mmol) of *p*-NA malonate, along with 64 mg (0.4 mmol) of AIBN were added. The polymerization tube was sealed using nitrogen gas and then inserted into an isothermal bath. The bulk polymerization reactions were carried out at 65 $^{\circ}$C for 24 h. The obtained product was dissolved in chloroform and the polymer solution filtered and added dropwise into ethyl ether to precipitate the copolymer. This procedure was extensively repeated until complete removal of the unreacted *p*-NA derivative chromophore and oligomers. The copolymers were recovered by filtration and dried under vacuum to constant weight. The reaction yield was approximately 47 % (1.49 g).

2.3. Polymer Characterization Assays

The FT-infrared spectra of the polymers and comonomers were obtained with a FT-IR Perkin-Elmer spectrometer 1000 using KBr pellets. The average molecular weights of the polymers were determined in THF solution by size exclusion chromatography (SEC) in a Waters model 515 pump chromatographer and UV 254 nm detector. The thermal properties of the polymers were evaluated in a Mettler DSC 825 analyzer at a heating rate of 10 $^{\circ}$C/min. The thermogravimetric analysis (TGA) of the samples was carried out in a Mettler TGA 851 analyzer at heating rate of 10 $^{\circ}$C/min under nitrogen. The casting polymer films

were obtained using a spinning process from a toluene solution. High quality waveguides were prepared using fused silica substrates through varying the parameters of the spin coating process, i.e. polymer solution concentration (wt %) (1 % $\leq$ cw $\geq$ 10 %), spinning speed (600 rpm $\leq$ ω $\geq$ 1500 rpm), and solvent type (chloroform or toluene). The films were further dried until the solvent was completely removed. The films thickness was measured with a TENCOR P-10 profilometer. The UV-Vis spectra of the chromophores and polymers in solution or in films were recorder with a UV-VIS-NIR Perkin Elmer 900 spectrophotometer. The intrinsic absorption coefficient α (λ) and the refractive index dispersion n (λ) of the waveguide with around 0.05 μm of thickness were calculated from the transmission and reflection spectra as described previously [18-20], with an experimental error of 5% due to that of the film thickness. The *p*-nitroaniline derivative chromophore content in the copolymers was estimated by the Lambert and Beer Law equation. The TE wave of probing radiation (with the electric vector parallel to the waveguide film) and TM wave (with the electric vector virtually perpendicular to the waveguide film) were investigated using the measured mode spectrum. The refractive index (n_{TE} and n_{TM}) of the waveguide with around 2 μm of thickness was measured. For this purpose, the TE polarized light from a He-Ne laser (633 nm) was coupled to the waveguide using a high index glass prism (LaSFN9, np = 1.84489). The coupling angle was adjusted until a guided mode was launched through the waveguide. The refractive indices were then calculated from the coupling angles following the method of Ulrich and Torge [21].

3. Results and discussion

The copolymers were synthesized by free radical copolymerization of styrene with the *p*-NA acryloyl or *p*-NA malonate chromophores, named PSPNA1 and PSPNA2, respectively. Homopolymerization of styrene was carried out as a blank reaction producing the parent PS, which was doped with different amounts of *p*-NA acryloyl or *p*-NA malonate. The IR spectra of the copolymers PSPNA1 and PSPNA2 and their respective *p*-NA acryloyl and *p*-NA malonate chromophores show IR absorptions in the range of 3125 to 2800 cm^{-1} due to the saturated carbon bonds and at 1600 to 1450 cm^{-1} due to C-C aromatic bonds (benzene ring). No absorptions related to the *p*-NA derivatives were detected in the infrared spectra of the copolymers since their content in the polymer backbone is quite low. Nevertheless, the *p*-NA derivative chromophores in the copolymers could be detected by UV-Vis spectrophotometry.

Table 1 summarizes the content of the *p*-nitroaniline derivative chromophores in the copolymer and in the mixture with PS, and the average molecular weights (M_n, M_w), and

glass transition (T_g) and decomposition (T_d) temperatures of the polymers. The *p*-NA acryloyl and *p*-NA malonate chromophores differ in terms of the type of vinyl group linked to the amino group which is less bulky in the former. Also, there is a carbonyl group between the amino and the double bond in the former. The PSPNA1 and PSPNA2 copolymers were produced with the same chromophore/styrene molar concentration (2.4 x 10^{-5} mol/g). The chromophore contents in the PSPNA1 and PSPNA2 copolymers were 7.8 x 10^{-6} and 6.8 x 10^{-6} mol/g, respectively, which correspond to around 30% of the initial chromophores concentration used. These values may be a consequence of a limiting factor related to the chromophores solubility in the styrene or in the reaction medium. The PSPNA1 copolymer has the same molecular weight as the parent PS (290,000 g.mol^{-1}) and PSPNA2 tended to a lower value (180,000 g.mol^{-1}) probably because the *p*-NA malonate chromophore acts as a chain transfer agent. Since the *p*-NA malonate has pendent methyl groups it can promote chain transfer during chain growing, by hydrogen abstraction, reducing the polymer molecular weight. The PS and its copolymers and the PS doped with *p*-nitroaniline derivative chromophores did not show differences in their T_g values, which were around 105 ^{o}C, since the incorporation of *p*-nitroaniline derivative chromophores into the backbone did not affect the chain mobility due to the low content. Hence, the PS doped with *p*-nitroaniline derivative chromophores can withstand the same temperatures of operation and manufacture as many copolymers. Nevertheless, the T_g values for the PS doped with *p*-nitroaniline derivative chromophores dropped to approximately 70 ^{o}C, indicating that this chromophore content affects the PS chain interactions and mobility. The T_d determined as the apex of the peak of the mass loss derivate curve was in the range of 404 to 417 ^{o}C for all samples analyzed. Additional peaks were observed for PSPNA1b presented as additional peak at 225 ^{o}C and PSPNA2a and PSPNA2b at approximately 290 ^{o}C attributed to partial decomposition of the chromophores [17].

Table 1: Molecular and thermal data of the parent PS, copolymers and doped PS.

Sample	Chromophore	Chromophore contend [mol/g]	M_w [x10^3 gmol^{-1}]	M_n [x10^3 gmol^{-1}]	T_g [^{o}C][a]	T_d [^{o}C][b]
Parent PS			290	70	105	404
PSPNA1	*p*-NA acryloyl	7.8 x10^{-6}	290	70	103	407
PSPNA1a	*p*-NA acryloyl	7.8 x 10^{-5}	290	70	71	414
PSPNA1b	*p*-NA acryloyl	1.4 x 10^{-4}	290	70	74	225/417
PSPNA1c	*p*-NA acryloyl	2.8 x10^{-4}	290	70	ND	ND
PSPNA2	*p*-NA malonate	6.8 x10^{-6}	180	40	103	405
PSPNA2a	*p*-NA malonate	6.8 x10^{-5}	290	70	78	284/413
PSPNA2b	*p*-NA malonate	1.4 x10^{-4}	290	70	64	295/414
PSPNA2c	*p*-NA malonate	2.8 x10^{-4}	290	70	ND	ND

Table 2 shows the spectral characteristics of the *p*-nitroaniline derivative chromophores, PSPNA1 and PSPNA2 copolymers analyzed in ethyl acetate or chloroform solution and PS doped with chromophores, including the maximum absorption (λ_{max}^{abs}), the molar extinction coefficient (ε_{max}), the maximum absorption ($\lambda_{max\ TE}$), and the maximum intrinsic absorption coefficient (α_{maxTE}). The *p*-NA acryloyl chromophore and respective copolymer PSPNA1, in ethyl acetate solution, and the *p*-NA malonate chromophore and its respective copolymer PSPNA2, in chloroform solution, show absorption regions in the range of 260 to 360 nm and 310 to 410 nm, respectively, characteristic of aniline derivatives [22] (Figure 2). The *p*-NA acryloyl chromophore and respective copolymer PSPNA1 have similarities in their spectra (Figure 2a), particularly in relation to the λ_{max}^{abs} value (Table 2), indicating that the polymer backbone with or without the chromophore structure is very similar. Hence, the *p*-NA acryloyl double bond saturation when copolymerized with styrene did not affect the electronic transitions and the chromophore absorbs almost at the same wavelength. In contrast to the *p*-NA malonate chromophore (Figure 2b), the copolymer PSPNA2 shows a hypsochromic shift of the maximum absorption from 362 to 375 nm. This result can be attributed to the double bond suppression in the *p*-NA malonate when it is bonded to the copolymer backbone, shifting to the blue wavelength. As expected, the *p*-nitroaniline derivative chromophores, and PSPNA1 and PSPNA2 copolymers, have molar extinction coefficients (ε_{max}) between 1.5 and 3.7 x 10^4 L mol^{-1} cm^{-1}, values which typically for allowed $\pi \rightarrow \pi^*$ transitions.

Table 2: Spectral characteristics of the copolymers.

Sample	λ_{max}^{abs} [nm][a]	ε_{max} [x10^4][c]	λ_{max} (TE) [nm]	α_{max} (TE) [10^3 cm^{-1}]
p-NA acryloyl	321	1.5	-	-
p-NA	362	3.7	-	-
PSPNA1	320	1.8	-	-
PSPNA1a	-	-	325	1.6
PSPNA1b	-	-	325	3.0
PSPNA1c	-	-	329	7.8
PSPNA2	355	3.3	-	-
PSPNA2a	-	-	362	5.4
PSPNA2b	-	-	362	10.2
PSPNA2c	-	-	362	17.7

[a] Ethyl acetate or chloroform solution.
[c] Molar extinction coefficient in L.mol^{-1}.cm^{-1} at the maximum of the band, 321 nm for *p*-NA acryloyl and 362 nm for p-NA malonate.
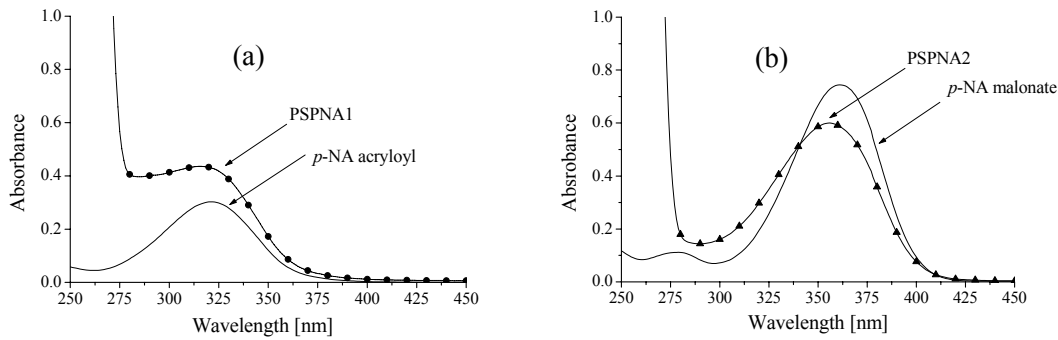
Figure 2: Absorption spectra of the PSPNA1 (3 g/L) and *p*-NA acryloyl chromophore (4 mg/L) (a) and of the PSPNA2 (3 g/L) and *p*-NA malonate chromophore (8 mg/L) (b) in ethyl acetate and chloroform solution, respectively.

The film characteristics are strongly affected by the film preparation parameters [23-25]. It was verified that solvents with a low boiling point, such as chloroform, produce spin coated PS films with a poor surface quality, having the appearance of orange peel [25]. Regarding the PS doped with *p*-nitroaniline derivatives, an increase in the chromophore content tends to saturate the polymer solution, causing its precipitation and leading to the chromophore particles being visible in the films. As a result, the films become opaque, with loss of the waveguide optical quality. Table 3 describes the visual quality of the prepared films. The highest amount of the two chromophores used to dope the PS, rendering thin films of around 0.05 μm without loss of optical quality, was 2.8×10^{-4} mol/g. However, for films with 2 μm of thickness, that require more concentrated solutions, the highest amount of chromophore able to dope PS was 1.4×10^{-6} or 2.8×10^{-4} mol/g for *p*-NA acryloyl or *p*-NA malonate, respectively.

Table 3: Optical thin films quality.

Chromophore-doped PS	Chromophore content [mol/g]	Film quality	
		0.05 μm	2.00 μm
p-NA acryloyl	1.4×10^{-6}	+	0
p-NA acryloyl	7.8×10^{-5}	+	-
p-NA acryloyl	1.4×10^{-4}	+	-
p-NA acryloyl	2.8×10^{-4}	+	-
p-NA acryloyl	1.4×10^{-3}	0	-
p-NA malonate	6.8×10^{-5}	+	+
p-NA malonate	1.4×10^{-4}	+	+
p-NA malonate	2.8×10^{-4}	+	+
p-NA malonate	1.4×10^{-3}	-	-

Figure 3 gives the absorption spectra, before subtraction of reflection losses [18], of the PS, PSPNA1 and PSPNA2 films, which show the presence of a strong band at 193 nm ascribed to the occurrence of electronic transitions in the PS. Absorptions related to the *p*-nitroaniline derivative chromophores were observed in the wavelength range scanned.

Figure 4 shows the refractive index dispersion $n(\lambda)$ of the PS, PSPNA1 and PSPNA2 films. The close similarity between the spectra indicates that the amounts, around 10^{-6} g/mol, of p-nitroaniline derivative chromophores attached to the copolymer chain are not sufficient to change the average refractive index of the medium.
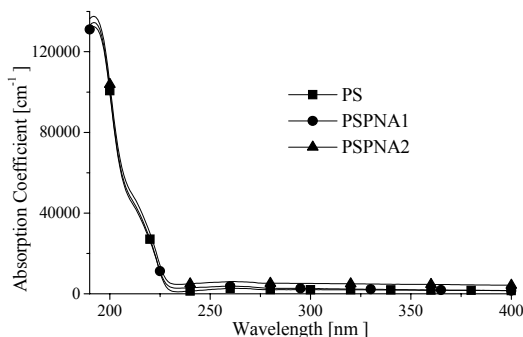

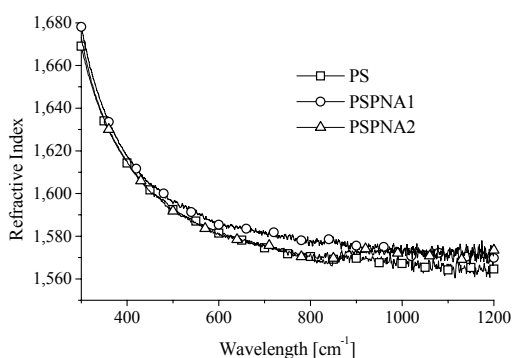Figure 3: Absorption spectra of PS, PSPNA1, PSPNA2 films (d ≅ 0.05 μm) before subtraction of reflection losses.

Figure 4: Dispersion of the refractive index of the PS, PSPNA1, PSPNA2 films (d ≅ 0.05 μm) measured by reflectometry.

The intrinsic absorption coefficients $\alpha(\lambda)$ of the PS and p-NA derivative-doped PS are given in Figure 5. As expected, the p-NA derivatives lead to an increase in the $\alpha(\lambda)$ value of the PS in the range of electronic transitions corresponding to each derivative. The electric field (E) of incident light is parallel to the film plane and the α_{maxTE} values increase for both chromophores (Table 2), particularly the p-NA malonate chromophore. This indicates that the dispersion of these molecules in the PS matrix increases the electron density due to donor-acceptor para disubstituted benzene compounds and the double bond of the N-malonate group, which favor the electronic resonance compared to N-acryloyl. Figure 6 shows the $n(\lambda)$ of PS and p-NA derivative-doped PS. The addition of p-NA acryloyl to the PS did not affected the polymer $n(\lambda)$, whereas the addition of p-NA malonate increased significantly the $n(\lambda)$ in the wavelength range analyzed, except in the case of PSPNA2a for which a slight decrease in the curve profile was observed compared

to the PS. The change in the $n(\lambda)$ value due to the addition of p-NA malonate to the PS can be attributed to N-malonate group being more susceptible to greater polarizability than the N-acryloyl group when submitted to an electric field. Furthermore, it can be seen that the intersection of the curves (Fig. 6b) occurs at 362 nm, which is related to the p-NA malonate λ_{max} absorption. The same should occur in the case of N-acryloyl at 325 nm, but this is not well resolved because of its lower molar absorptivity.
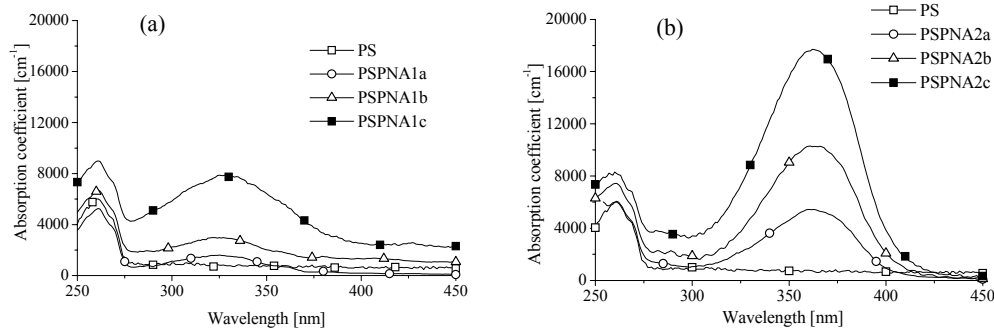

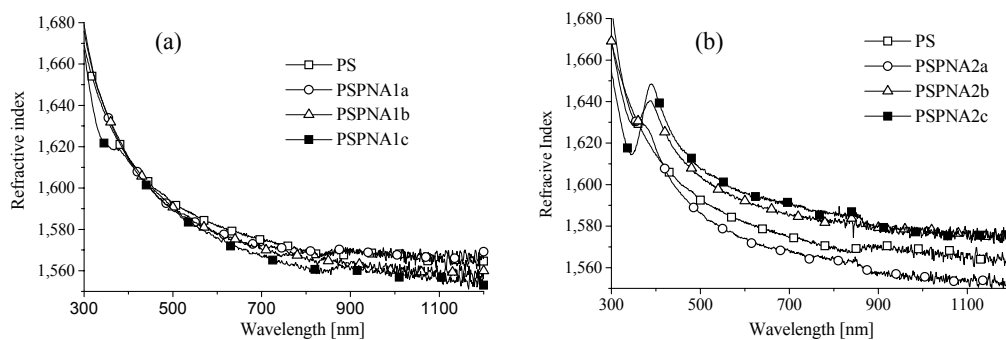Figure 5: Absorption spectra of PS and p-NA acryloyl (a) and p-NA malonate (b) doped PS films (d $\cong$ 0.05 μm).

Figure 6: Dispersion of the refractive index of PS and p-NA acryloyl (a) or p-NA malonate (b) doped PS films (d $\cong$ 0.05 μm) measured by reflectometry.

The refractive index (n_{TE} and n_{TM}) and birefringence ($\Delta n = n_{TE} - n_{TM}$) values of the PS and p-NA malonate-doped PS are given in Table 4. The birefringence values indicate the level of optical anisotropy in the film, which is the difference between the refractive indices of orthogonal planes of polarization or a measure of the polymer molecular orientation. Birefringence of PS film waveguides was found to be negative, which is in agreement with results reported in the literature [26]. The decrease in Δn values is normally caused by a more random orientation of phenyl rings in the PS. It seems that the intrinsic anisotropic orientation of PS phenyl groups was disturbed by p-NA malonate chromophore addition.

Table 4: Refractive index and birefringence of PS and p-NA malonate-doped PS.

Sample	n_{TE} [632.8nm]	n_{TM} [632.8nm]	Δn [632.8nm]
PS	1.578	1.582	- 0.004
PSPNA2a	1.584	1.587	- 0.003
PSPNA2b	1.586	1.588	- 0.002
PSPNA2c	1.588	1.590	- 0.002

4. Conclusions

New copolymers of styrene with N-acryloyl p-nitroaniline or N-diethyl methylenemalonate p-nitroaniline chromophores were obtained. The glass transition and decomposition temperatures and the refractive index profile of copolymers were similar to those of the parent PS. The PS doped with *p*-nitroaniline derivative chromophores had lower glass transition temperatures and a different refractive index profile compared with PS. The addition of the *p*-nitroaniline derivative chromophore to PS increased the average electron density of the medium. Thin films of the copolymers and *p*-nitroaniline derivative-doped PS were obtained by the spin coating method. Good optical quality waveguide films could be obtained from *p*-NA derivative-doped PS.

Acknowledgements

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