[illegible]

[illegible]

Optical Materials

An International Journal on the Physics and
Chemistry of Optical Materials and their
Applications, including Devices

EDITOR-IN-CHIEF
A. M. Srivastava

[illegible]

Optical Materials

Journal info

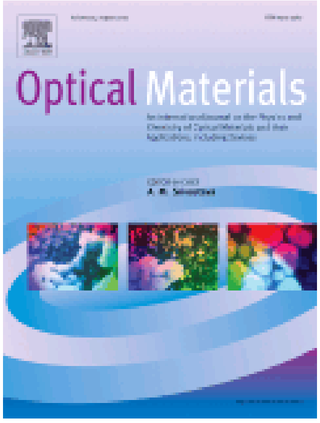
Editor-in-Chief

Editors

Associate Editors

Advisory Board

ISSN: 0925-3467



(https://www.sciencedirect.com/science/journal/09253467)
Visit journal homepage >

Submit your paper >

Guide for authors >

Track your paper >

Order journal >

View articles >

Editorial board >

Browse journals (/... > Optical Materia... > Abstracting an...

Abstracting and Indexing

- Chemical Abstracts
- Current Contents - Engineering, Technology & Applied Sciences
- EI Compendex Plus
- Engineering Index
- INSPEC
- Scopus

Optical Materials

Volume 32, Issue 11

Pages 1397-1558 (September 2010)

Previous vol/issue Next vol/issue

Full text access

IFC (Editorial Board)

Page IFC

Invited Article

Research article ○ Abstract only

Organic–inorganic hybrid materials towards passive and active architectures for the next generation of optical networks

R.A.S. Ferreira, P.S. André, L.D. Carlos
Pages 1397-1409

Purchase PDF Article preview

Regular Articles

Research article ○ Abstract only

Anisotropy of thermal conductivities in non- and Mg-doped near-stoichiometric $LiTaO_3$ crystals

Masaru Nakamura, Shunji Takekawa, Kenji Kitamura
Pages 1410-1412

Purchase PDF Article preview

Research article ○ Abstract only

Investigating the response of As_2S_3-based SERS substrates

Christopher J. Rowlands, Lei Su, Stephen R. Elliott
Pages 1413-1416

Purchase PDF Article preview

Research article ○ Abstract only

Ln^{3+}-enhanced blue fluorescence from novel excimer of 1,8-naphthalimide-conjugated PAMAM

Jianguo Tang, Hui Yang, Jixian Liu, Yao Wang, ... Zhen Huang
Pages 1417-1422

Purchase PDF Article preview

Research article ○ Abstract only

Electrodeposited ZnCdO thin films as conducting optical layer for optoelectronic devices

B. Marí, M. Tortosa, M. Mollar, J.V. Boscà, H.N. Cui
Pages 1423-1426

Purchase PDF Article preview

Research article ○ Abstract only

Fabrication and investigation of 1D and 2D structures in $LiNbO_3$ thin films by pulsed laser ablation

F. Meriche, A. Boudrioua, R. Kremer, E. Dogheche, ... N. Boutaoui
Pages 1427-1434

Research article ○ Abstract only

Luminescence properties and structure of Eu^{2+} doped $KMgPO_4$ phosphor

Suyin Zhang, Yanlin Huang, Hyo Jin Seo

Pages 1545-1548

Purchase PDF Article preview

Research article ○ Abstract only

Raman active phonon and crystal-field studies of Yb^{3+} doped $NdVO_4$

S. Jandl, Y. Lévesque, V. Nekvasil, M. Bettinelli

Pages 1549-1552

Purchase PDF Article preview

Research article ○ Abstract only

Femtosecond filamentation in chalcogenide glasses limited by two-photon absorption

Ivan Blonskyi, Viktor Kadan, Oleh Shpotyuk, Mihail Iovu, Ihor Pavlov

Pages 1553-1557

Purchase PDF Article preview

ISSN: 0925-3467

Optical Materials
Volume 32, Issue 11, September 2010, Pages 1526-1531

Waveguide optical properties of polystyrene doped with *p*-nitroaniline derivatives

M.R. Becker [a], V. Stefani [b], R.R.B. Correia [c], C. Bubeck [d], M. Jahja [d], M.M.C. Forte [a]

Show more

https://doi.org/10.1016/j.optmat.2010.06.015 Get rights and content

Abstract

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.

Previous

Keywords

Polystyrene; *p*-Nitroaniline derivative; Spin coating; Refractive index; Waveguide

Recommended articles Citing articles (4)

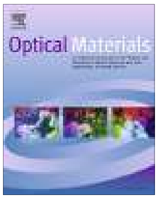
View full text

Optical Materials 32 (2010) 1526–1531

Contents lists available at ScienceDirect

Optical Materials

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



Waveguide optical properties of polystyrene doped with *p*-nitroaniline derivatives

M.R. Becker [a,*], V. Stefani [b], R.R.B. Correia [c], C. Bubeck [d], M. Jahja [d], M.M.C. Forte [a]

[a] *UFRGS, Engineering School, Laboratory of Polymeric Materials, Av. Bento Gonçalves, 9500 – Box Mail 15010, 91501-970 Porto Alegre, RS, Brazil*
[b] *UFRGS, Chemical Institute, Organic Chemistry Department, Av. Bento Gonçalves, 9500 – Box Mail 15003, 91501-970 Porto Alegre, RS, Brazil*
[c] *UFRGS, Physics Institute, Physics Department, Av. Bento Gonçalves, 9500 – Box Mail 15051, 91501-970 Porto Alegre, RS, Brazil*
[d] *Max Plank Institute for Polymer Research, Ackermannweg, 10, 55128 Mainz, Germany*

ARTICLE INFO

Article history:
Received 20 March 2009
Received in revised form 18 June 2010
Accepted 21 June 2010
Available online 27 July 2010

Keywords:
Polystyrene
p-Nitroaniline derivative
Spin coating
Refractive index
Waveguide

ABSTRACT

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.

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 [1–5]. The refractive index profile is the most important characteristic in a waveguide and defines the properties of the optical waveguide as an informational system element and thus determines the performance of the whole planar device [6–8]. 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 [9–11]. A film of syndiotactic polystyrene [12] in the nanoporous crystalline δ form has been studied for the detection of chloroform vapor at very low concentration. Refractive index variation due to chloroform sorption by the polymer has been used as a transduction property. In addition, Mohamed and co-workers [13] investigated different acrylate formulations from cyclized acrylic copolymers comparatively with fluorinated acrylate. The thermooptic coefficients, dn/dT, of the polymers are as high as the order of 10^{-4}, which is comparable with those of available optical polymers. Cyclized acrylates have higher dn/dT values than fluorinated acrylate.

The modification of the properties of these polymers by adding chromophores [14,15] into the polymer or attaching them to the backbone has attracted considerable interest [16]. 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 is a cornerstone chromophore for optical applications and its derivatives, allowing the improvement of the physicochemical properties, are highly demanded as prospective materials. Tagaya et al. [17] have reported a method for compensating for the birefringence of optical polymers by doping them with birefringent strontium carbonate ($SrCO_3$) crystals. The *p*-nitroaniline derivative chromophores [18] 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 [19,20].

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 investigated. Also, polystyrene doped with *p*-nitroaniline derivatives was assessed for application as a waveguide. The refractive indices of the thin polymeric films produced by the spin coating method were evaluated.

---

[*] Corresponding author. Tel.: +55 51 3308 6272; fax: +55 51 3308 7304.
E-mail address: mrbeck@portoweb.com.br (M.R. Becker).

0925-3467/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2010.06.015

2. Experimental

2.1. Materials

Polymerization-grade styrene supplied by INNOVA S.A. (Brazil) was used as received. The *p*-nitroaniline derivative *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 [21]. 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 °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 (M_w and M_n) of the polymers were determined in THF solution at room temperature by size exclusion chromatography (SEC) in a Waters model 515 pump chromatographer. Three columns in series (SD Plus 10^6, 10^4 and 500) and an UV 254 nm detector were used. The thermal properties of the polymers were evaluated in a Mettler DSC 825 analyzer at a heating rate of 10 °C/min. The thermogravimetric analysis (TGA) of the samples was carried out in a Mettler TGA 851 analyzer at heating rate of 10 °C/min under nitrogen. Thin polymer films were obtained by spin coating from a toluene solution filtered through a 0.5 or 5 mm micropore filter. High quality waveguides were prepared using freshly cleaned fused silica substrates (35 mm × 25 mm × 1 mm) through varying the parameters of the spin coating process, i.e. polymer solution concentration (wt.%) ($1\% \leqslant cw \geqslant 10\%$), spinning speed ($600\ \mathrm{rpm} \leqslant \omega \geqslant 1500\ \mathrm{rpm}$), and solvent type (chloroform or toluene). The films were dried under vacuum at 45 °C, 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 recorded 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 thickness were calculated from the transmission and reflection spectra as described previously [22–24], 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 using a standard calibration procedure with *p*-NA acryloyl or *p*-NA malonate in ethyl acetate or chloroform solutions, respectively. The TE wave of the laser beam (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 film was pressed against the base plane of a symmetric prism mounted on a precision rotary table. 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 [25].

3. Results and discussion

The chemical structures of the copolymers synthesized by free radical copolymerization of styrene with the *p*-NA acryloyl or *p*-NA malonate chromophores, named PSPNA1 and PSPNA2, respectively, are shown in Fig. 1. 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 copolymers obtained are amorphous and showed good solubility in acetone, chloroform and THF. The infrared 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 3125–2800 cm^{-1} due to the saturated carbon bonds and at 1600–1450 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 (PSPNA1a-c and PSPNA2a-c), 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 (2.4×10^{-5} mol/g). The chromophore contents in the PSPNA1 and PSPNA2 copolymers were 7.8×10^{-6} and 6.8×10^{-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

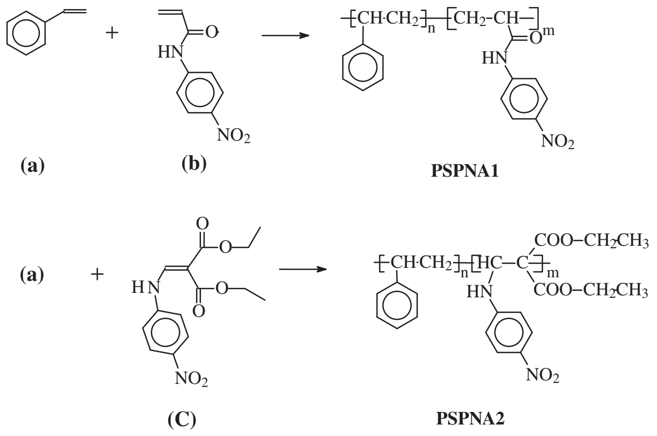


Fig. 1. Synthetic route for the styrene/*p*-NA derivative copolymers from (a) styrene with (b) *p*-NA acryloyl or (c) *p*-NA malonate chromophores.

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

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

ND: not determined.
[a] DSC at a heating rate of 10 °C/min.
[b] DTG at a heating rate of 10 °C/min under nitrogen.
[c] *p*-Nitroaniline derivative chromophores in the copolymer.
[d] *p*-Nitroaniline derivative chromophores in the mixture with PS.

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 °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 °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 404–417 °C for all samples analyzed. Additional peaks were observed for PSPNA1b presented as additional peak at 225 °C and PSPNA2a and PSPNA2b at approximately 290 °C attributed to partial decomposition of the chromophores [21].

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^{abs}_{max}), the molar extinction coefficient (ε_{max}), the maximum absorption (λ_{maxTE}), 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 260–360 nm and 310–410 nm, respectively, characteristic of aniline derivatives (Fig. 2). The absorption spectra of the *p*-nitroaniline derivative chromophores PSPNA1 and PSPNA2 are very similar in shape to those containing only a single *p*-NA unit [26]. This indicates that the conjugation of the *p*-nitroaniline derivative chromophores do not result in a pronounced change in the HOMO–LUMO characteristics of the derivatives, leading to a similar band gap value and structure, as reported in literature [27]. Additionally, the orientational polarization signal may be the same magnitude otherwise the spectra would be quite different. No additional long wavelength absorption bands indicative of intramolecular electron exchange interactions between the *p*-NA chromophoric units are apparent. The *p*-NA acryloyl chromophore and respective copolymer PSPNA1 have similarities in their

Table 2
Spectral characteristics of the copolymers.

Sample	λ^{abs}_{max} (nm)[a]	ε_{max} ($\times 10^4$)[b]	λ_{max} (TE) (nm)	α_{max} (TE) (10^3 cm^{-1})
p-NA acryloyl	321	1.5	–	–
p-NA malonate	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.
[b] 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.

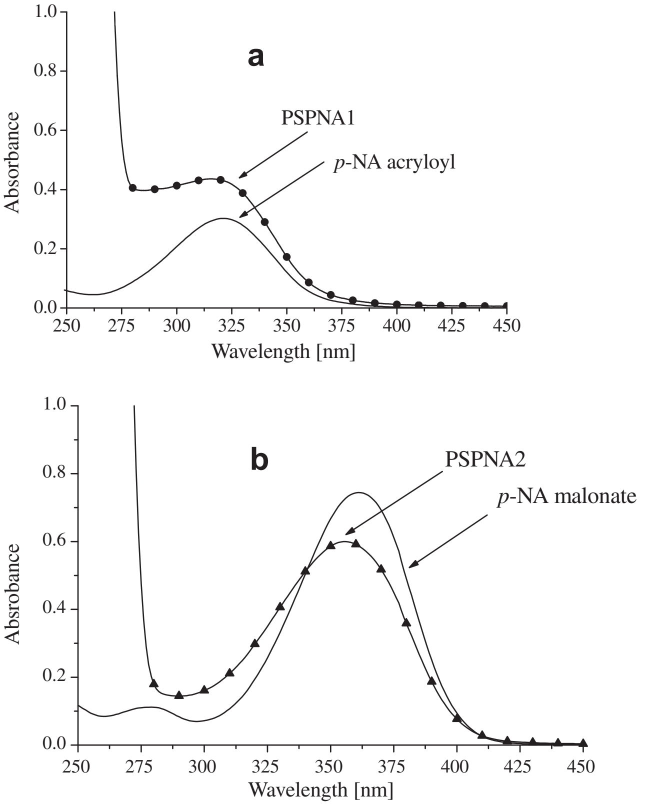


Fig. 2. Absorption spectra of the PSPNA1 (3 g/L) and *p*-NA acryloyl chromophore (4 mg/L) (a) and of the PSPNA2 (3 g/L) and *p*-NA malonate chromophore (8 mg/L) (b) in ethyl acetate and chloroform solution, respectively.

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}	–	–

Clear appearance (+), opaque (–) and poor appearance (0).

spectra (Fig. 2a), particularly in relation to the $\lambda_{\max}^{\text{abs}}$ 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 (Fig. 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 ($\varepsilon_{\max}$) between 1.5 and 3.7×10^4 L mol^{-1} cm^{-1}, values which typically for allowed $\pi \rightarrow \pi^*$ transitions.

The film characteristics are strongly affected by the film preparation parameters [28–30]. In order to produce films with good quality, the solution concentration, spinning speed, and solvent type were systematically varied. Several solvents have been reported to be suitable for PS, including methylene chloride [31], chloroform [1], toluene [15], and chlorobenzene [32]. 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 [30]. 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 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.

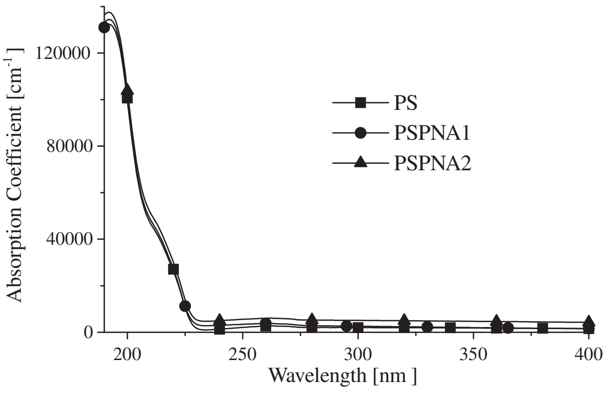


Fig. 3. Absorption spectra of PS, PSPNA1, PSPNA2 films ($d \cong 0.05$ μm) before subtraction of reflection losses.

Fig. 3 gives the absorption spectra, before subtraction of reflection losses [22], 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. Fig. 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.

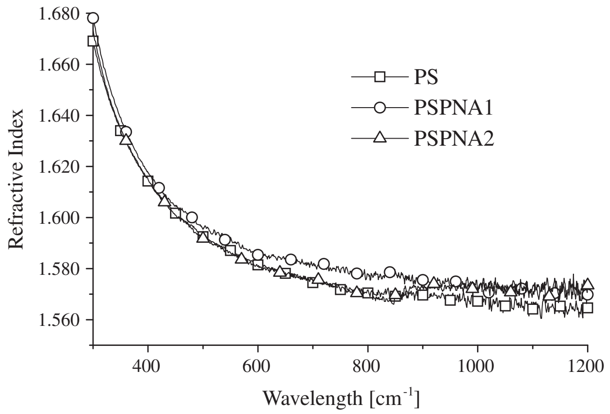


Fig. 4. Dispersion of the refractive index of the PS, PSPNA1, PSPNA2 films ($d \cong 0.05$ μm) measured by reflectometry.

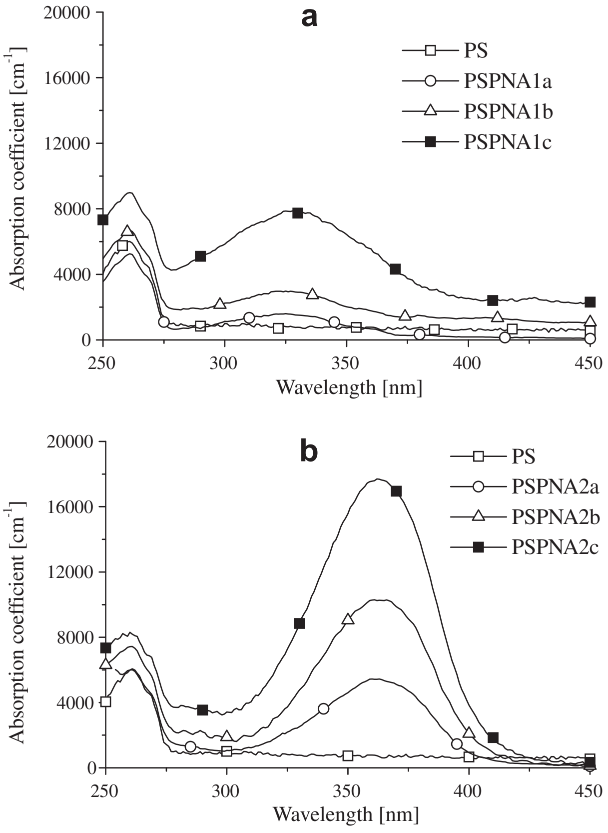


Fig. 5. Absorption spectra of PS and *p*-NA acryloyl (a) and *p*-NA malonate (b) doped PS films ($d \cong 0.05$ μm).

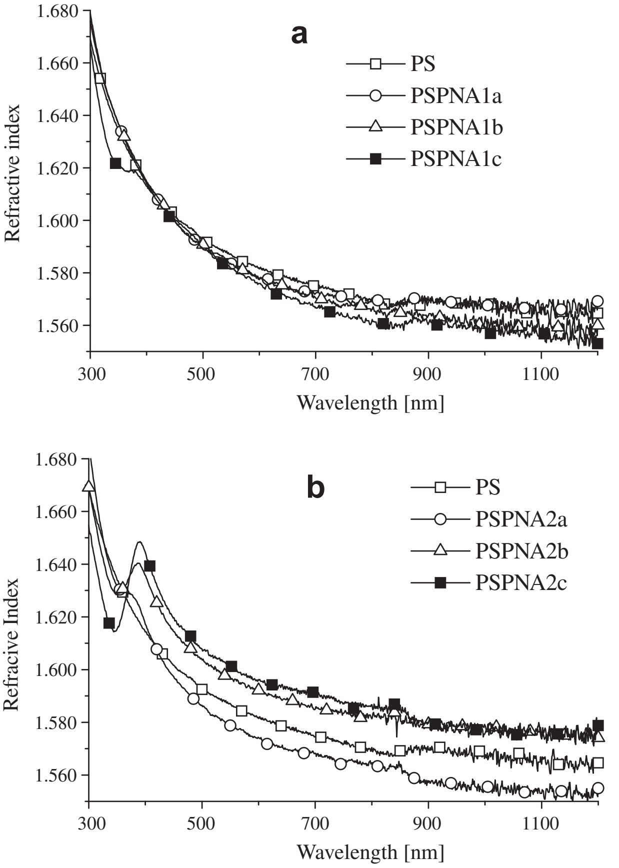


Fig. 6. Dispersion of the refractive index of PS and *p*-NA acryloyl (a) or *p*-NA malonate (b) doped PS films ($d \cong 0.05$ μm) measured by reflectometry.

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

Sample	n_{TE} (632.8 nm)	n_{TM} (632.8 nm)	Δn (632.8 nm)
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

The intrinsic absorption coefficients α (λ) of the PS and *p*-NA derivative-doped PS are given in Fig. 5. As expected, the *p*-NA derivatives lead to an increase in the α (λ) value of the PS in the range of the dye absorptions. 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. Fig. 6 shows the n (λ) of PS and *p*-NA derivative-doped PS. The addition of *p*-NA acryloyl to the PS did not affected the polymer n (λ), whereas the addition of *p*-NA malonate increased significantly the n (λ) 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 (λ) 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.

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 [33]. 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.

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 linear optical properties were modified according to the doping chromophore and respective concentration. 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

The authors thank the Brazilian Agency CNPq for support and scholarships, Max Planck Institute in Mainz for perform the investigations of the thin films and G. Herrmann and W. Scholdei for help with the experiments.

References

[1] S. Agan, F. Ay, A. Kocabas, A. Aydinli, Appl. Phys. A 80 (2005) 341.
[2] H. Liang, B. Chen, J. Xu, W. Su, F. Guo, B. Guo, Q. Zhang, Z. Zheng, H. Ming, Mater. Lett. 59 (2005) 4030.
[3] W.A. Daoud, M.L. Turner, React. Funct. Polym. 66 (2006) 13.
[4] K.H. Smith, R.H. Selfridge, S.M. Schultz, D.J. Markos, B.L. Ipson, Opt. Exp. 12 (2004) 354.
[5] H. Ma, A.K.Y. Jen, L.R. Dalton, Adv. Mater. 14 (2002) 1339.
[6] S.K. Sharma, K.N. Tripathi, Optik 114 (2003) 106.
[7] A. Stump, U. Gubler, C. Bosshard, Opt. Lett. 30 (2005) 1333.
[8] R. Horváth, H.C. Pedersen, N. Skivesen, D. Selmeczi, N.B. Larsen, Opt. Lett. 28 (2003) 1233.
[9] K. Tamaki, H. Takase, Y. Eriyama, T. Ukachi, J. Photopolym. Sci. Technol. 16 (2003) 639.
[10] A.V. Tomov, A.V. Khomchenko, Technol. Phys. Lett. 30 (2004) 747.
[11] S. Park, K. Cho, C. Choi, J. Colloid. Interface Sci. 258 (2003) 424.
[12] M. Giordano, M. Russo, A. Cusano, G. Mensitieri, Sens. Actuators B 107 (2005) 140.
[13] R. Mohamed, N. Razali, A.A. Ehsan, S. Shaari, Sci. Technol. Adv. Mater. 6 (2005) 375.
[14] F. D'Amore, M. Lanata, S.M. Pietralunga, M.C. Gallazzi, G. Zerbi, Opt. Mater. 24 (2004) 661.
[15] V. Švorčık, M. Prajer, I. Huttel, V. Rybka, V. Hnatowicz, J. Plešek, Mater. Lett. 59 (2005) 280.
[16] Y. Liu, A. Jiang, L. Xiang, J. Gao, D. Huang, Dyes Pigm. 45 (2000) 189.
[17] A. Tagaya, H. Ohkita, M. Muco, R. Sakaguchi, Y. Koike, Science 8 (2003) 812.
[18] A.M. Moran, A.M. Kelley, S. Tretiak, Chem. Phys. Lett. 367 (2003) 293.
[19] A.N. Rashid, K. Kirschbaum, R.K. Shoemaker, J. Mol. Struct. 785 (2006) 1.
[20] O.Y. Borbulevych, R.D. Clark, A. Romero, L. Tan, M.Y. Antipin, V.N. Nesterov, B.H. Cardelino, C.E. Moore, M. Sanghadasa, T.V. Timofeeva, J. Mol. Struct. 604 (2002) 73.
[21] M.R. Becker, Doctor Theses, Federal University of Rio Grande do Sul, 2007.

[22] A. Mathy, K. Ueberhofen, R. Schenk, H. Gregorius, R. Garay, K. Muellen, C. Bubeck, Phys. Rev. B 53 (1996) 4367.
[23] F. Fitrilawati, M.O. Tjia, S. Pfeiffer, H.H. Hörhold, A. Deutesfeld, H. Eichner, C. Bubeck, Opt. Mater. 21 (2002) 511.
[24] K. Koynov, A. Bahtiar, T. Ahn, R.M. Cordeiro, H.H. Hörhold, C. Bubeck, Macromolecules 39 (2006) 8692.
[25] R. Ulrich, R. Torge, Appl. Opt. 12 (1973) 2901.
[26] W. Schuddeboom, J.M. Warman, H.A.M. Biemans, E.W. Meijer, J. Phys. Chem. 100 (1996) 12369.
[27] E. Kavita, N. Sundaraganesan, S. Sebastian, Indian J. Pure Appl. Phys. 48 (2010) 20.
[28] C. Ton-That, A.G. Shard, D.O.H. Teare, R.H. Bradley, Polymer 42 (2001) 1121.
[29] Y.-Y. Lua, X. Cao, B.R. Rohrs, D.S. Aldrich, Langmuir 23 (2007) 4286.
[30] K.E. Strawhecker, S.K. Kumar, Macromolecules 34 (2001) 4669.
[31] W.M. Prest, D.J. Luca, J. Appl. Phys. 50 (1979) 6067.
[32] G.K. Singh, V.K. Sharma, A. Kapoor, K.N. Tripathi, Opt. Laser Technol. 33 (2001) 445.
[33] W.M. Prest, D.J. Luca, J. Appl. Phys. 51 (1980) 5170.