

ARTICLES

Improvements of the Poly(vinyl cinnamate) Photoresponse in Order to Induce High Refractive Index Variations

Imane Assaid,[†] Dominique Bosc,^{*,†} and Isabelle Hardy[‡]

Groupement d'Intérêt Scientifique "FOTON", CCLO, Centre Commun Lannionnais d'Optique, Laboratoire d'Optronique UMR CNRS 6082 ENSSAT and Département d'Optique ENST-Bretagne, ENSSAT BP 447, 6 rue de Kérampont, 22305 Lannion Cedex, France

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Under UV irradiation, poly(vinyl cinnamate) (PVCi) films undergo cross-linking due to [2 + 2] photocycloaddition between cinnamoyl groups. Consequently, electronic configuration of lateral polymer groups changes and also leads to the drop of the refractive index in the visible range. This mechanism is studied with regards to the level of the electronic absorption of cinnamate centered at 278 nm. It acts on refractive index by shifting the absorption UV band. Most of the time, this influence vanishes in the near infrared region (NIR). It is due to antagonist phenomena acting at the expense of the index lowering. The causes analysis leads us to optimize the irradiation spectrum, providing higher index contrasts between irradiated and nonirradiated area. We show that strong index changes can be achieved in PVCi film, up to 2.5×10^{-2} even in the NIR, enabling us, for example, to perform optical photoprinting waveguides for telecommunication wavelengths (1300–1550 nm).

Introduction

Poly(vinyl cinnamate), (PVCi), was formerly a well-known polymer exploited as a negative photoresist.¹ As a matter of fact, the cross-linking occurs under deep UV irradiation of this polymer, leading to the insolubility² of the material. Photolithography processes take advantage of this property. The cross-linking is due to the [2 + 2] photocycloaddition³ between an excited cinnamoyl groups of one polymer chain and a ground state cinnamoyl group of another. By the way, the refractive index is lowered because of changing the electronic configuration of lateral polymer groups. This index modification arises from the bleaching of electronic absorption band of cinnamate in the UV region. The cycloaddition causes the decrease of this band (maximum centered at 278 nm), and its shift to the far UV and consequently changes the imaginary part of the refractive index. As a result, the change of the index even part acts on the value of the refractive index for upper wavelengths. Nevertheless, the influence on refractive index is less and less as the wavelength moves off. Currently, we are working to make use of this phenomenon to print optical paths such as channel optical waveguides in PVCi films. A lot of works have proved the interest to perform fully polymer optical waveguides^{4–8} and hybrid silica–polymer waveguides.⁴ Usually, methods to create channel waveguides require multistep process involving photolithography, etching and annealing.^{5–6} A photoprinting process makes unnecessary an etching step. This advantage can be also combined to easier connecting operations and vertical integrated optical functions. To perform channel optical waveguide some

conditions have to be fulfilled. The main requirement concerns refractive index difference (Δn) between the core index and the cladding index of the waveguide. In many cases, for this index level, a Δn , slightly higher than 0.005, is enough to ensure the confinement of optical mode and its propagation. However, it can be advantageous to get higher Δn for reducing the waveguide size in order to increase the density of optical waveguides onto a single substrate for example. For this reason, Δn as high as possible will be the aim of this study. Another requirement is concerning the wavelengths use of the waveguides. For telecommunication applications, the wavelengths are chosen in the spectrum region between 1300 and 1600 nm. That means Δn must be effective for these wavelengths. A few years ago, we performed one of the first works on PVCi waveguides where good index contrast (or Δn) was achieved in the red light region (632.8 nm),⁹ since no investigation had been made in the near-infrared region (NIR) for optical waveguides. Nevertheless, index contrast is generally much weaker in NIR than in visible region, because chromatic dispersion of refractive index decreases index difference far from electronic absorption bands. Furthermore, some antagonist phenomena act at the expense of index lowering. This paper points out the influence of the irradiation spectrum on the sensitivity of PVCi in order to enhance the index contrast in the NIR. We will show what adjustment of irradiation spectrum can significantly increase the Δn both in the visible and near-infrared regions.

Experimental Section

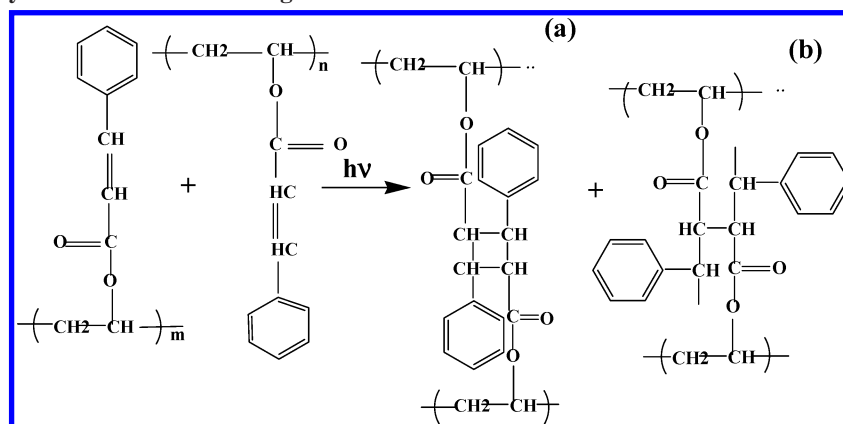
Materials. Polymers, which can undergo image wise light induced reactions, are of high research interest and technological importance. A classical example of photosensitive polymers is based on the cinnamoyl photoreactive groups (Scheme 1). The

* Corresponding author. E-mail: dominique.bosc@enssat.fr.

[†] Laboratoire d'Optronique UMR CNRS 6082 ENSSAT, France.

[‡] Département d'Optique ENST-Bretagne, France.

SCHEME 1. Two Ways of PVCi Cross-Linking



polyvinylcinnamate (PVCi) is purchased from Aldrich Inc. The solvents, such as chloroform, hexane and 1,1,2-trichloroethane, are provided by Aldrich. Siltronix supplies the silicon substrate with refractive index 3.4 and Heraeus those of silicate with 1.47 refractive index. The glass slides for UV filter are supplied by Corning Inc. with 1.51 refractive index.

Purified Poly(vinyl cinnamate). The PVCi is made by cinnamoylation of poly(vinyl alcohol). Often, the cinnamoylation reaction is incomplete and the product may include unreacted hydroxyls. The hydroxyl groups are undesirable for telecom applications because they present a broad absorption band in the near-infrared region.

So, we purified the crude PVCi as described in ref 10 in which the authors show the effect of the purification on the molar mass, the molecular size distribution and the hydroxyl content and consequently on the image quality of the photoresist. This process removes the greater part of hydroxyl groups and enhances the physical film quality.

PVCi is purified¹⁰ by dissolving 5 g in 50 mL of chloroform. The suspension is heated overnight on a bath of water at 50 °C. After cooling, solution is added to 300 mL of hexane with stirring, to precipitate the polymer. Then it is filtered and washed several times with hexane before drying for 24 h at 60 °C. The yield of the pure product is 96%.

We have made analysis by size exclusion chromatography (SEC) and they show that the molar mass of the crude PVCi is 100 000 and the molecular size distribution is 1.9. After purification, the molar mass and molecular size distribution slightly change (110000 and 1.94 respectively). Furthermore, the IR-TF analysis performed, indicate a decrease of hydroxyl content after purification.

The dry powder is dissolved in trichloro-1,1,2-ethane to yield a solution of about 230 g/L enabling the film formation by spin coating onto various slides and followed by a post bake at 130 °C for 30 min.

Thin Films Realization. A spin coating technique is used to prepare thin films from a solution on various substrates. The substrate is rotated about an axis through its center and perpendicular to its surface, at typical rotation rate of several thousand rpm. Solution containing the photoactive polymer is then dropped onto the center of the substrate and a thin film is formed as the solution spreads over the substrate and the solvent rapidly evaporates. Thin films of a few micrometers thick (between 1 and 10 μm) are prepared. This range of thickness is suitable for integrated optics and waveguide applications.

Irradiation Proceedings. Ultraviolet light irradiations are performed with medium-pressure mercury lamps emitting at various wavelengths (UV ELC 4001 from Electro-Lite Corp.).

We use a 312 nm receiver to detect the power and the energy of exposure. Figure 1 shows the absorption spectrum in the UV–visible region of the receiver we used. Also, in some cases, one or two superimposed glass slides are used as filters. Figure 2 shows the absorption spectra of the filters. Above 300 nm, these slides are transparent, however below 300 nm they allow filtering more or less the deep UV light.

Characterization Techniques. A spectrometer Perkin-Elmer Lambda 900 is used to measure thickness and absorption of polymer film. The Lambda 900 is a versatile spectrometer operating ultraviolet, visible, and near-infrared spectral ranges. Film thickness can be deduced from interferometry spectrum in the visible region. Measurements of PVCi electronic absorption are performed with film samples coated on a silica plate. In some cases, to analyze weak absorption above 340 nm and to avoid interferences, we use as a substrate, special glass slides having the same index as PVCi ($n = 1.6$).

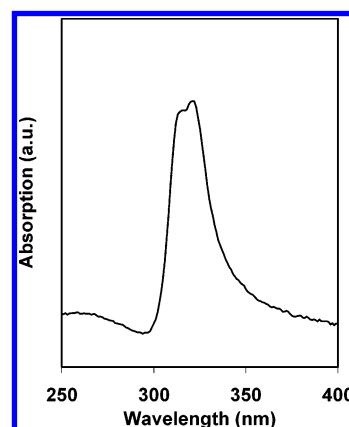


Figure 1. Absorption spectrum of the receiver used in the study.

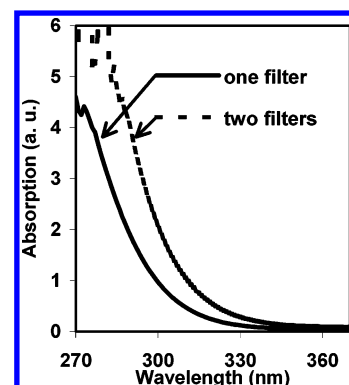


Figure 2. Absorption spectrum of the filters in the UV–visible region.

To exhibit the evolution of the polymer specific vibration bands, FT-IR spectra are carried out with a double-beam infrared spectrometer. The polymer is dispersed in a tablet of potassium bromide. KBr tablets are prepared by grinding the polymer sample (2 mg) with KBr (100–200 mg) and compressing the whole into a transparent tablet. The polymer sample and KBr should be heated to a temperature of 40 °C before grinding under an infrared lamp to avoid condensation of atmospheric moisture.

Refractive index is measured using the m-lines method, based on prism–evanescent wave coupling.¹¹ A prism (with index much higher than that of polymer) is applied on the polymer film to be characterized. Convergence of a monochromatic beam onto the prism base creates an evanescent field in total reflection conditions. Depending on the injection angle of the light beam, evanescent field can excite propagation modes in the guide so that, beam propagates inside the film. For other angles, the beam is reflected at the film–air interface and drops to a photo-detector. Examining the prism reflected light, we can see “black lines” (so-called m-lines), when laser beam is guided into the film. By measuring m-lines angles, we determine the effective index of the planar guide, which can be known better than $\pm 2 \times 10^{-4}$. For example, the refractive index of nonirradiated PVCi is 1.6090 at 632.8 nm and 1.5850 at 1550 nm.

Results and Discussion

Photo-Cross-Linking. Polyvinylcinnamate (PVCi) is the earliest synthetic photopolymer.¹² Its design, a polyvinyl backbone with cinnamoyl side chains, is conceived in the hope that photocycloaddition between polymer-bound cinnamoyl groups would cross-link adjacent macromolecules. The PVCi is cross-linked by photoaddition between an excited cinnamoyl group of one polymer chain and a ground-state cinnamoyl group of another. In this case, carbonyl and phenyl groups provide favorable polarization to the double bond. Thus, the photo-reaction of cinnamoyl groups takes place easily to form photo-cross-linking, however the actual cross-linking mechanism of this system is still uncertain. Scheme 1 visualizes cross-linking as producing an extended network in the polymer as described by Hephner.¹ The main response of PVCi to photons is believed to be dimerization (Scheme 1a) at least 65%. Films of polyvinylcinnamate, when exposed to UV light, are completely insoluble in almost all common solvents.

UV Absorption and Refractive Index Relationship. The purpose of this study consists of producing refractive index difference in a PVCi film. For dielectric materials we know that index is generally ruled by the Lorentz–Lorenz law, expressed for polymers by the Gladstone–Dale expression (eq 1)

$$\frac{n^2 - 1}{n^2 + 2} = \frac{d}{M} R_m \quad (1)$$

where M is the molar mass of monomer unit, d is its density, n is the refractive index, and R_m is the monomer molar refractivity. This equation gives parameters, which control the refractive index, particularly molar refractivity, which is wavelength dependent as well as refractive index, and the density of material. All things being equal, index varies as density. Furthermore, molar refractivity depends on the structure and on the electronic configuration of monomer molecule. These features generally cause absorption bands in the UV region. On the other hand, the refractive index is a complex number (eq 2) where its imaginary part is a function of absorption, so that,

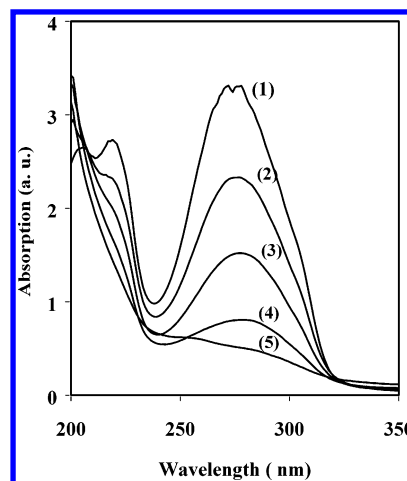


Figure 3. UV absorption spectrum of PVCi film before irradiation (1) and irradiation for $E = 0.23 \text{ J/cm}^2$ (2), $E = 1.23 \text{ J/cm}^2$ (3), $E = 6.23 \text{ J/cm}^2$ (4), and $E = 30.23 \text{ J/cm}^2$ (5) (energy measured at 312 nm).

its value is depending on the location and the intensity of the bands.

$$n = n' + in'' \quad (2)$$

Some modifications of the material may influence for the intensity and the position of an absorption band and shift it to a longer (bathochromic effect) or a shorter (hypsochromic effect) wavelength. As a result, the refractive index can change at wavelengths even far from the absorption band.

The absorption of PVCi results from absorption of groups containing the cinnamoyl function. Thus, the $\text{O}=\text{CH}-\text{CH}=\text{CH}-$ group absorbs at around 215 nm. Since this group is linked to a phenyl group, absorption peak is moved to longer wavelength of about 15 nm. On the other hand, by introducing an auxochromic group, like oxygen, the absorption band center is still red shifted (bathochromic shift). In PVCi all these groups yield an absorption band centered at 278 nm.

Under UV irradiation, the absorption peak at 278 nm disappeared, corresponding to the opening of the double bond $\text{C}=\text{C}$, and the absorption band is shifted to the far UV (hypsochromic shift) around 200 nm and corresponds to phenyl and carbonyl group absorption. Therefore, the photobleaching¹³ process, by shifting the absorption band to the far UV, induces a lessening of refractive index, even far from the UV band, in red and infrared wavelengths (in telecom applications spectrum range). Figure 3 shows a typical absorption spectrum of a thin film of polyvinylcinnamate (PVCi) before and after UV irradiation.

Improvements of the Refractive Index Control. For the purpose of photoprinting single-mode optical waveguides in PVCi film, we aim to obtain a large index contrast in the near-infrared region (1300 and 1550 nm) between no irradiated and irradiated areas for a thickness film of typically a few micrometers. With this material, an index contrast slightly higher than 0.005 is enough to ensure the confinement of optical mode and its propagation. Nevertheless, to reduce the optical losses in curvature,¹⁴ it is important to increase more the refractive index difference between core and cladding of the waveguide. For these reasons, in this study, for single mode waveguide applications, we target refractive index differences between 1×10^{-2} and 3×10^{-2} .

First, we observe that a refractive index difference (contrast) of 1.7×10^{-2} can be achieved in the red region (632.8 nm)

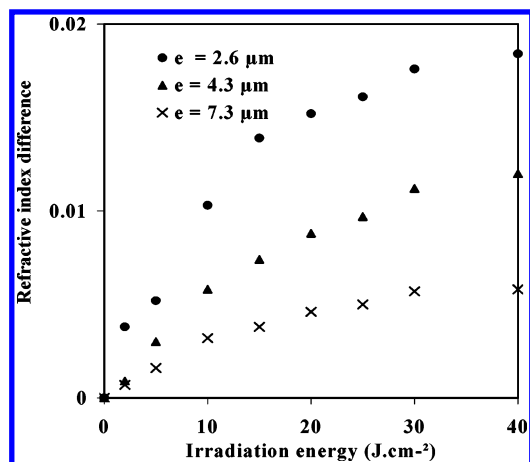


Figure 4. Variation of index contrast at 1550 nm for different thickness films as a function of irradiation energy.

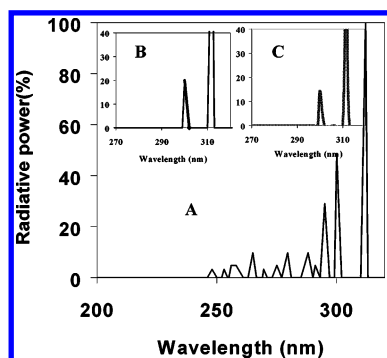


Figure 5. Emission spectrum intensity of the mercury lamp, normalized at 312 nm, without a filter (A), with one filter (B), with two filters (C).

under 40 J cm^{-2} for a $5 \mu\text{m}$ thick PVCi film. Figure 4 shows the first results of contrast measured at 1550 nm for several thickness films. It is noticed that the refractive index difference after UV irradiation depends strongly on the film thickness. For example, the contrast is equal to 1.8×10^{-2} for a film thickness of about $2.6 \mu\text{m}$, instead of 5.8×10^{-3} for a $7.3 \mu\text{m}$ thick film. At 1300 nm, we achieve similar results. Moreover, we note that the film thickness slightly declines under UV irradiation (a few percent). As a result, the thickness reduction should produce an increase of the refractive index. This phenomenon runs counter to the required drop of the refractive index and could limit the index lowering of the photobleaching effect.

With a view to improve the index contrast, we try to suppress opposite phenomena to the index lowering. After UV irradiation, they can be due to film compactness and higher absorption band appearance.

Thus, a discoloration (yellowing) of PVCi film is observed sometime after UV exposure. The yellowing of PVCi film can be explained by deep UV damage. We take note that some samples remain uncolored after UV exposure through UV filter. For these reasons, we have to know the irradiation spectrum (normalized at 312 nm) of our mercury lamp with and without filter (Figure 5). We find that the optical filter hinders deep UV, below 300 nm. We note in Figure 5 that the addition of two filters just makes slightly weaker the peak emission at around 300 nm.

The use of a filter also lessens the intensity level for the entire spectrum. For example the lamp intensity, measured with the 312 nm receiver, drops from 50 to 12 mW cm^{-2} , without and with a filter, respectively. So, to exhibit if it is an effect of intensity or an effect of filtering, UV exposures are implemented

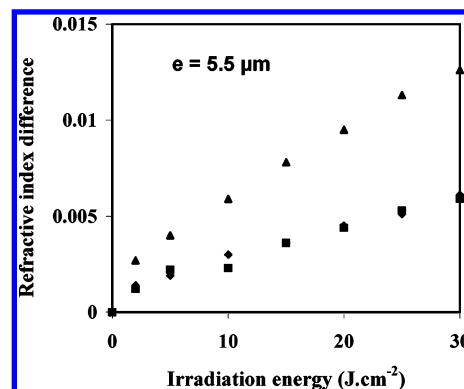


Figure 6. Effect of power density of the mercury lamp for refractive index difference at 1550 nm: (◆) 50 mW/cm^2 without a filter; (■) 12 mW/cm^2 without a filter; (▲) 12 mW/cm^2 with one filter (film thickness $e = 5.5 \mu\text{m}$).

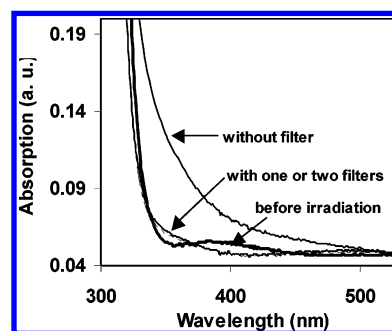


Figure 7. Absorption spectrum of PVCi close to the absorption band (at $\lambda_{\text{max}} = 278 \text{ nm}$) in the UV-visible region.

with or without a filter, and under various UV light intensity (in moving lamp away). Figure 6 exhibits that for the same irradiation energy measured at 312 nm, the index contrast is higher only with the filter onto the film. For instance, for 40 J cm^{-2} irradiation energy, the contrast grows up to 1.26×10^{-2} with a filter and 12 mW cm^{-2} lamp intensity, instead of 5.9×10^{-3} without a filter for 50 and 12 mW cm^{-2} .

To highlight the yellowing of the PVCi film and its contrary effect on the refractive index, we have carefully studied the UV spectrum of PVCi (Figure 7) above 340 nm, close to the absorption band. Without any filter, the absorption of the irradiated sample clearly increases between 300 and 500 nm unlike samples irradiated with filters. This amount, related to the discoloration of PVCi film, distinguishes colored centers and increases the refractive index.

As a result, we can expect the more efficient the deep UV filtering, the higher the contrast. It seems also that the 300 nm emission reduces the effect on the contrast; thus, it is better with two filters than with one (up to 2.5×10^{-2} at 1550 nm) (Figure 8). Currently it is difficult to filter more than the 300 nm emission without weakening all the wavelengths too.

With regards to these new exposure conditions, we examine the index contrast behavior at 1550 nm (Figure 9). We get now the same contrast whatever the thickness, and it reaches 2.5×10^{-2} after 25 J cm^{-2} . However, beyond 30 J cm^{-2} , the refractive index of irradiated PVCi increases, that could be due to higher compactness phenomenon of PVCi film. The compactness reaches 15% for every thickness after 30 J cm^{-2} irradiation energy.

According to results in Figures 7–9, we can put forward the following idea: it is necessary to use one filter at least to avoid

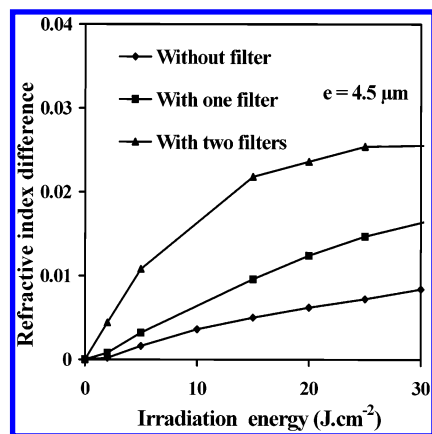


Figure 8. Comparison of the contrast measured on a $4.5 \mu\text{m}$ thick film at 1550 nm with three kinds of UV spectra.

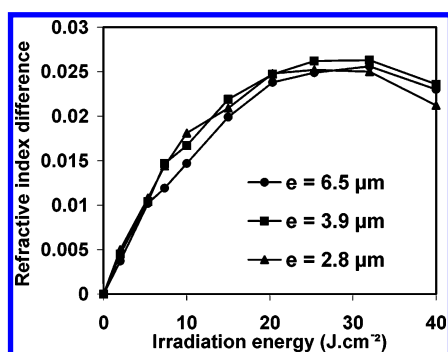


Figure 9. Variation of the contrast at 1550 nm for different thickness (e) as a function of exposure energy under filtered irradiation.

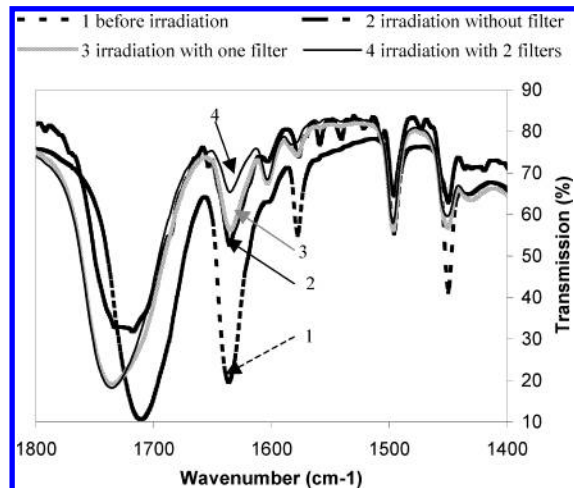


Figure 10. Typical IR spectrum of PVCi before and after UV exposure: influence of filtering during irradiation on the $-\text{CH}=\text{CH}-$ absorption band.

the appearance of colored centers, and to optimize the index contrast, two filters are needed.

Optical filtering also improves the photoreaction efficiency of cinnamoyl groups. The disappearance of $\text{C}=\text{C}$ absorption (Figure 10) at 1640 cm^{-1} is followed vs irradiation energy. It is clear that absorption band at 1640 cm^{-1} vanishes under UV irradiation. Furthermore, this absorption band decreases more, since samples are irradiated through two filters. In the same way, we note that the conversion yield of the chromophore, observed at 278 nm , rises until 10 J cm^{-2} , whereupon it stabilizes above 0.95 since two filters are used. Previously, with one filter or without a filter, the yield stabilized around 0.8 . We can conclude that the yield of double bond opening is better

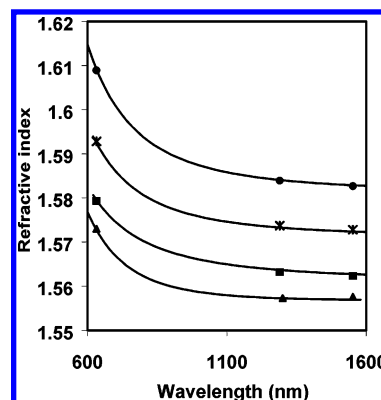


Figure 11. Chromatic dispersion of a PVCi film (thickness $e = 5 \mu\text{m}$) before and after UV irradiation [$(\bullet) E = 0 \text{ J/cm}^2$; $(\times) E = 40 \text{ J/cm}^2$ without a filter; $(\blacksquare) E = 40 \text{ J/cm}^2$ with one filter; $(\blacktriangle) E = 40 \text{ J/cm}^2$ with two filters].

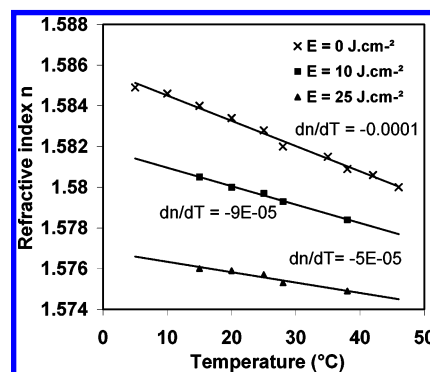


Figure 12. Variation of refractive index at 1550 nm as a function of temperature before and after UV irradiation.

since irradiation at 300 nm is less. However, Figure 9 indicates there is an optimum contrast, probably due to the compactness of the film.

By using several light sources with the m-lines method, we can measure the chromatic dispersion of the index. Figure 11 shows the chromatic dispersion of PVCi film since thickness is $5 \mu\text{m}$, before and after several UV irradiations. Because of the moving away of the absorption band, the refractive index of PVCi and also the contrast before and after UV exposure decrease from the red to infrared region (eq 2). Nevertheless, a contrast as high as 2.5×10^{-2} is achieved at 1550 nm , which is the main wavelength for optical telecommunication.

By taking advantage of our thermocontrolled m-lines method, we can also measure the refractive index at several temperatures before and after UV irradiation. Thereby, we obtained easily the thermal sensitivity coefficient (dn/dT) of the PVCi refractive index. Figure 12 gives thermo-optical coefficients (dn/dT) of PVCi, before UV exposure ($\text{dn}/\text{dT} = 1 \times 10^{-4}$), or after 10 and 25 J cm^{-2} of UV filtered exposure (dn/dT is divided by 2). The former is similar to the coefficient of polymethacrylate polymers⁶ and, after UV exposure, the strong lowering can be due to the free volume shrinkage after cross-linking.

In summary, we have studied the refractive index change under UV exposure. The hypsochromic effect of the electronic absorption band of PVCi leads to a decrease of the refractive index. This phenomenon is also quite effective in the NIR region, enabling the photoprinting of optical waveguides for telecom applications. By adjusting the UV spectrum, antagonist phenomena, such as colored centers, can be suppressed and by way, intrinsic index variation into the film raises up to 2.5×10^{-2} . So far, reported contrasts of around 8×10^{-3} have been achieved in polymers with photoinitiator,¹⁵ and compared to

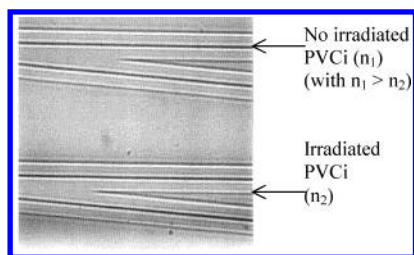


Figure 13. Photoprinted waveguide example on a 5 μm thick PVCi film.

mineral glasses or silica ($\Delta n \sim 10^{-2}$),^{16–18} the PVCi photo-induced index contrast is significantly improved. This large range of contrasts enables us to build higher density optical circuits. For example, Figure 13 is a picture of PVCi waveguides we are now able to produce.

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