Optical waveguide fabrication using a polymeric azine containing the 3-dodecylthiophene moiety

Claudio Amari,^a Corrado Pelizzi,^a Giovanni Predieri,*^a Silvia Destri,*^b William Porzio,^b Heiko Einsiedel,^c Bernhard Menges^c and Silvia Mittler-Neher*^c

"Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale delle Scienze, I-43100 Parma, Italy

^bIstituto di Chimica delle Macromolecole del C.N.R., Via E. Bassini 15, I-20133 Milano, Italy ^cMax-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

New polymeric azines, DOZ and DOPh, containing the 3-dodecylthiophene moiety, have been obtained by the condensation reactions of 2,5-diformyl-3-dodecylthiophene with hydrazine and *p*-diaminobenzene, respectively. Their average molecular masses depend on the preparation conditions. Using DOZ polymers, which are completely soluble in common organic solvents, we were able to demonstrate channel waveguide formation and function. The waveguide losses could be separated into intrinsic absorption losses and scattering contributions.

Optical switching in waveguide geometries has attracted interest in recent years. Various classes of materials, e.g. semiconductors, glasses and polymers, have been investigated for this purpose.1 Among these, polymeric materials are very attractive because they can be tailored by chemists to improve desired properties.² In fact a high $\chi^{(3)}$ value is desirable for optical switching at low input powers and, in addition, the material should be processable and photobleachable so that channel waveguides can be fabricated. It should also exhibit low linear losses and a relatively high refractive index, n, to assure a good field confinement in the waveguide.³ It has been shown that polythiophenes are a class of materials which offer most of the desired functions.^{4,5} Nevertheless, the formation of channel waveguides has not been demonstrated so far, because of high waveguide losses,⁶ mainly attributable to small crystallite dimensions which give rise to pronounced scattering phenomena.⁷ Another class of promising non-linear optical materials is that of azines and polyazines, eventually substituted with donor and/or acceptor groups.8

Following our current interest in functionalized Schiff base derivatives,⁹ we focused our attention on polymeric species containing the thiophene ring and the C=N linkage, with the aim of producing new metal complexing agents and/or novel materials for non-linear optics (NLO). In fact, it has been shown recently¹⁰ that certain hydrazone derivatives are an efficient class of NLO materials. In a previous paper,¹¹ we obtained a novel series of air-stable, deeply coloured polyazines by the condensation reactions of hydrazine with 2,5-diformyl or 2,5-diketo derivatives of thiophene and 3-alkylthiophenes. The resulting polymeric materials were largely insoluble in common organic solvents, with the exception of the butyl derivatives, which were almost completely soluble in light chlorinated solvents.

In order to improve the solubility characteristics of these Schiff base polymers, we have synthesized 2,5-diformyl-3dodecylthiophene and studied its reactions with hydrazine and *p*-diaminobenzene. The condensation reactions afford two new polymeric materials containing the azomethine linkage, DOZ and DOPh, respectively.





In this paper we demonstrate the possibility of using DOZ to fabricate channel waveguides and to separate the linear losses into intrinsic absorptions and scattering losses, having found the optimal spectral region which is nearly free of absorption.

Experimental

General procedures and materials

All the organic and organometallic starting materials were commercially available (Aldrich) and were used as received. The solvents were reagent grade (C. Erba) and, when necessary, were dried by standard techniques before use. Manipulations of air-sensitive compounds were carried out under dry nitrogen by means of standard Schlenk glassware.

Microanalyses (C, H, N, S) were made with a C. Erba EA 1108 automatic equipment. FTIR spectra were recorded in the range 4000–400 cm⁻¹ using a Nicolet 5PC spectrometer. UV–VIS spectra were performed using a Cary 2300 instrument. ¹H and ¹³C NMR spectra were obtained with a Bruker AMX 400 instrument in deuteriated chloroform. XRD measurements were carried out at room temperature using a computer-controlled Philips diffractometer (Cu-K\alpha radiation).

Size exclusion chromatography (SEC) was carried out with a Waters system consisting of a 600E pump, a 717 autosampler, a 410 differential refractometer and a 490 UV detector (wavelength 254 nm). The column set was composed of two Waters styrangel (10^4-10^5 , pore size 500 Å). The experimental conditions consisted of a mobile phase (THF), at room temperature, flow rate 1 ml min⁻¹, a sample concentration of 1 mg ml⁻¹ and an injection volume of 150 µl. Each solution was filtered through a 0.45 µm filter. The calibration was performed with polystyrene standard, the molecular mass of which ranged from 500 to 10^6 .



Scheme 1 Reagents and conditions (1) $C_{12}H_{25}MgBr$, [N1(dppp)Cl₂], Et₂O, (11) BuL1, TMEDA, hexane, THF, (11) DMF, HCl (aq), NaHCO₃

Preparations

The polymeric Schiff bases DOZ and DOPh were prepared starting from 2,5-diformyl-3-dodecylthiophene, whose synthesis is outlined in Scheme 1

The reaction of 3-bromothiophene with dodecylmagnesium bromide, in the presence of the bis(diphenylphosphino)propane (dppp) nickel(II) complex, gave the 3-alkylthiophene derivative in high yield ¹² The material was dilithiated in positions 2 and 5 using butyllithium, in the presence of tetramethylethylenediamine (TMEDA), in hexane–THF solution By reaction with dimethylformamide, the 2,5-diformylation took place, producing the lithium salt of the diamide derivative, which was transformed into the 2,5-dicarboxy derivative ¹³ Finally, this compound was treated by condensation¹¹ with hydrazine and *p*-diaminobenzene to obtain the Schiff base polymers DOZ and DOPh, and with aniline to produce DOA as a useful model compound for the polymeric species



3-Dodecylthiophene

C₁₂H₂₅Br (0 3 mol) in dry Et₂O (100 ml) was added dropwise over 1 h to a stirred suspension of Mg (0 32 mol) in the same solvent (80 ml) kept at 0 °C by an ice bath, under a nitrogen atmosphere The reaction mixture was stirred overnight and was then added dropwise over 2 h to an Et₂O solution (100 ml) containing 3-bromothiophene (0 3 mol) and [Ni(dppp)Cl₂] (0 005 mol) The mixture was heated at reflux for 3 h and then added to an excess of water (0 61) The organic layer was collected, dried and reduced in volume with a rotary evaporator 3-Dodecylthiophene was obtained by distillation under reduced pressure (133 °C, 0 8 mbar, yield 70%), ¹H NMR (CDCl₃) δ 7 36 (dd, H₅, 1 H), 7 10 (dd, H₄, 1 H), 7 06 (m, H₂, 1 H) [³J(4,5) 4 92, ⁴J(2,5) 2 93, ⁴J(2,4) 1 24 Hz], 2 83 (t, α -CH₂, 2 H), 1 85 (quint, β -CH₂, 2 H), 1 52 (br m, γ - λ -CH₂, 18 H), 1 13 (t, ω -CH₃, 3 H)

2,5-Diformyl-3-dodecylthiophene

A hexane solution (1 6 mol, 100 ml) of butyllithium was added to a mixture of TMEDA (0 16 mol) and 3-dodecylthiophene (0 08 mol) in dry hexane (150 ml) After 10 min a white powder precipitated from the orange solution The suspension was stirred for 30 min at 40 °C and then heated at reflux for 30 min more After addition of dry THF (150 ml), the suspension was cooled at -70 °C An excess of DMF (0 27 mol) was added dropwise under nitrogen over 10 min The reaction mixture was left to reach room temperature and the obtained solution was poured into a 3% aqueous HCl solution (11), under vigorous stirring and kept below 0 °C After neutralization with sodium hydrogen carbonate, the organic layer was extracted several times with dichloromethane and dried with sodium sulfate Distillation under reduced pressure (170 °C, 0 1 mbar) gave a pure product (80% yield), MS (CI) m/z 309 [M+1]⁺, 281 [M+1-CO]⁺, 253 [M+1-2CO]⁺, FTIR ν/cm^{-1} 1690, 1669 (CO stretch), ¹H NMR (CDCl₃) δ 999 (s, 2-HCO, 1 H), 9 82 (s, 5-HCO, 1 H), 7 58 (s, ring H₄, 1 H), 2 87 (t, α-CH₂, 2 H), 1 57 (quint, β-CH₂, 2 H), 1 09 (m, γ-λ-CH₂, 18 H), 0 71 (t, ω-CH₃, 3 H), ¹³C NMR (CDCl₃) δ 1830 (2-HCO), 182 5 (5-HCO), 151 8 (C₂), 147 5 (C₅), 142 9 (C₃), 137 2 (C₄), 31 5 (α-CH₂), 30 8 (β-CH₂), 29 3-28 9 (γ-ι-CH₂), 28 0 (κ-CH₂), 22 3 (λ-CH₂), 13 7 (ω-CH₃)

2,5-Bis(phenyliminomethyl)-3-dodecylthiophene (DOA)

In a 100 ml three-necked round-bottomed flask, equipped with a magnetic stirrer and a refrigerator, 2,5-diformyl-3-dodecylthiophene (0 004 mol) and aniline (0 008 mol) were dissolved in toluene (50 ml) The mixture was heated at reflux for 24 h, then was cooled and poured into an aqueous solution of sodium hydrogen carbonate The organic phase was dried with sodium sulfate and reduced to a small volume by a rotary evaporator The light orange product was separated by flash chromatography (yield 90%) using hexane-ethyl acetate (80 20) as the eluent mixture, mp 40 °C, MS (CI) m/z 459 $[M+1]^+$, FTIR v/cm⁻¹ 1590 (C=N stretch), ¹H NMR $(CDCl_3) \delta 863$ (s, 5-HC=N, farther from the side chain, 1 H), 850 (s, 2-HC=N, nearer to the side chain, 1 H), 742 (m, phenyl rings, 10 H), 7 33 (s, thiophene ring H_4 , 1 H), 2 85 (t, α -CH₂, 2 H), 1 73 (quint, β -CH₂, 2 H), 1 40 (m, γ - λ -CH₂, 18 H), 0 90 (t, ω-CH₃, 3 H)

Polymer DOZ

Polycondensation between hydrazine and 2,5-diformyl-3-dodecylthiophene was carried out under different experimental conditions, as summarized in Table 1 The procedure described below concerns the samples DOZ3–DOZ6 (DOZ6 was used in the optical experiments), nevertheless it applies also to the other samples, with the modifications indicated in Table 1

In a 100 ml three-necked round-bottomed flask, equipped with a magnetic stirrer and a refrigerator, 2,5-diformyl-3dodecylthiophene (0011 mol) and hydrazine (98%, 0011 mol) were dissolved in ethanol (40 ml) Some drops of acetic acid were added to the refluxing reddish-yellow solution, which darkened immediately The mixture was heated at reflux for 24 h, then was cooled and poured into an aqueous solution of sodium hydrogen carbonate The red precipitate, insoluble in 96% H₂SO₄, but completely soluble in chloroform, was examined by SEC, exhibiting an average molecular mass, Mr, of 21 1 × 10³ with a dispersity, η , of 3 5 (DOZ3 from Table 1) By increasing the reaction time (72 h), a polymer showing a narrower dispersity (18) was obtained (DOZ6) In contrast, a curing procedure consisting of thermal treatment below 150 $^\circ C$ produced materials exhibiting larger η values (DOZ4,5) DOZ3 elemental analysis, found C, 71 51, H, 9 96, N, 8 10, S, 10.61%, the polymer DOZ of infinite length, $C_{18}H_{18}N_2S$, requires C, 71 05, H, 9 27, N, 9 20, S, 10 53%, FTIR ν/cm^{-1} 2923, 2852 (CH stretch), 1598 (HC=N stretch), 1464 (C=C stretch), 841 (CH out-of-plane bend), UV-VIS ring $\lambda_{max}(CH_2Cl_2)$ 491 nm, ¹H NMR ($CDCl_3$) δ 885 (br s, 5-HC=N, farther from the side chain, 1 H), 8 68 (br s, 2-HC=N, nearer to the side chain, 1 H), 7 30 (br s, ring H₄, 1 H), 2 83 (br, α -CH₂, 2 H), 1 70 (br, β -CH₂, 2H), 1 23 (br, γ - λ -CH₂, 18 H), 0 89 (br, ω-CH₃, 3 H)

Polymer DOPh

Polycondensation between *p*-diaminobenzene and 2,5-diformyl-3-dodecylthiophene was carried out under different experimental conditions as summarized in Table 2 The procedure described below concerns the sample DOPh1, nevertheless it

Table 1 Reaction conditions and SEC data for the polymeric compounds DOZ1-DOZ11, obtained by condensation between 2,5-diformyl-3-dodecylthiophene and hydrazine

species	hydrazine (%)	solvent	catalyst, time/h	$M_{ m r} imes 10^{3a}$	η^b	
DOZ1	98%	toluene	CF ₃ COOH, 24	1.5	1.3	
DOZ2	98%	toluene	amberlite, ^c 24	2.0	1.5	
DOZ3	98%	EtOH	CF ₃ COOH, 24	21.1	3.5	
$DOZ4^{d}$			no cat., 24	34.6	4.9	
$DOZ5^{d}$		_	no cat., 72	256.1	60.7	
DOZ6	98%	EtOH	CF ₃ COOH, 72	22.0	1.8	
DOZ7	98%	Pr ⁿ OH	CF ₃ COOH, 24	12.1	2.2	
DOZ8	anhvdr.	EtOH	no cat., 24	3.8	2.7	
DOZ9	anhydr.	EtOH	CF ₃ COOH. 24	17.8	4.5	
DOZ10	anhydr.	EtOH	amberlite. ^c 24	7.5	2.2	
DOZ11	anhydr.	THF	CF ₃ COOH, 36	11.5	2.8	

^a Average molecular mass from SEC, referred to polystyrene. ^b Dispersity. ^c Strongly acidic (sulfonic acid functionality) resin. ^d Polymers obtained by thermal treatment (120 °C) of DOZ3 under reduced pressure (0.2 mbar).

Table 2 Reaction conditions and SEC data^{*a*} for the polymeric compounds DOPh1–DOPh4 and BUPh, obtained by the condensation of 2,5diformyl-3-dodecylthiophene and 2,5-diformyl-3-butylthiophene, respectively, with *p*-diaminobenzene

species	3-chain	solvent	catalyst, time/h	$M_{ m r} imes 10^{3a,b}$	η ^c	
DOPh1	dodecyl	toluene	CF ₃ COOH, 24	10.1	3.2	
DOPh2	dodecyl	toluene	no cat., 24	23.6	3.5	
DOPh3	dodecyl	toluene	amberlite, 24	8.7	3.3	
DOPh4	dodecyl	DMF	LiCl, 24	18.2	3.6	
BUPh	butyl	toluene	no cat., 24	6.2	2.3	

^a Chloroform extraction. ^b Average molecular mass from SEC, referred to polystyrene. ^c Dispersity.

applies also to the other samples, with the modifications indicated in Table 2.

In a 100 ml three-necked round-bottomed flask, equipped with a magnetic stirrer and a refrigerator, 2,5-diformyl-3and dodecylthiophene (0.005 mol) *p*-diaminobenzene (0.005 mol) were dissolved in toluene (40 ml). By adding some drops of acetic acid to the refluxing solution, the colour turned dark red. The mixture was heated at reflux for 24 h, then was cooled and poured into an aqueous solution of sodium hydrogen carbonate. The red precipitate was extracted with chloroform in a Kumagawa apparatus leaving an insoluble residue (ca. 30%); the soluble fraction was examined by SEC, exhibiting an average molecular mass of 10.1×10^3 with a dispersity of 3.2 (DOPh1 from Table 2). The aromatic diamine was reacted also with the 3-butylthiophene-2,5-dicarboxaldehyde¹¹ giving the polymer BUPh.

DOPh1: elemental analysis, found: C, 75.25; H, 8.90; N, 6.95; S, 8.03%; the polymer DOPh of infinite length, $C_{24}H_{32}N_2S$, requires: C, 75.74; H, 8.48; N, 7.36; S, 8.43%; FTIR ν/cm^{-1} : 2921, 2850 (CH stretch), 1593 (HC=N stretch), 1504, 1492, 1461 (C=C ring stretch), 829, 717 (CH out-of-plane bend); UV-VIS: λ_{max} (CH₂Cl₂) 550 nm; ¹H NMR (CDCl₃) δ : 8.65 (br s, 5-HC=N, farther from the side chain, 1 H), 8.52 (br s, 2-HC=N, nearer to the side chain, 1 H), 7.25 (br, rings, 5 H), 2.87 (br, α-CH₂, 2 H), 1.65 (br, β-CH₂, 2 H), 1.25 (br, γ-λ-CH₂, 18 H), 0.85 (br, ω-CH₃, 3 H).

Optical measurements

All sample preparation steps were performed in a class 100 clean room. The DOZ6 sample was dissolved in chloroform (15 min at 30 °C in an ultrasonic bath) as an 8 mass% solution. Before film formation by spin coating, the solution was filtered twice (1 and 0.2 μ m pore sizes).

For the determination of the refractive index of the material and the waveguide losses a standard waveguide characterization setup was used.^{4,14} The polarized laser beam was coupled into a slab waveguide ($4.2 \mu m$) by a grating, which was fabricated holographically and ion-milled into the fused silica substrate.¹⁵ The image of the streak, taken with an IR-sensitive video camera (Electrophysics) was digitalized using commercial software (Image-Pro Plus). The resulting intensity profile was fitted to a decreasing exponential function and the loss in dB cm⁻¹ was calculated. In order to determine the refractive index (n = 1.627 at 1150 nm) the coupling angles were measured by investigating the transmission dips.

For the bleaching experiment a polymer film of thickness 850 nm was spin-coated on top of a fused silica slide. For the channel waveguide formation the sample was then placed in a contact mask aligner (Cobilt) and irradiated for 72 h. The coupling into the channel waveguide structures was done by a prism, since this polyazine is not too soft for this. The prism could be removed without damaging the film.

The absorption spectrum from 700 to 2400 nm was taken of a sample of thickness 48 μ m with a photothermal beam deflection (PBD) spectrometer.^{16,17} The sensitivity of this setup was 10⁻² cm⁻¹. The absorption coefficients for the wavelengths where the loss measurements were performed were calculated in dB cm⁻¹ and subtracted from the waveguide losses. This difference value gives the amount of scattered light. The PBD image was taken with the same setup, which was altered slightly for the imaging.¹⁸ Transmission absorption spectra were taken with a Perkin Elmer 19 spectrometer.

Results and Discussion

Chemical characterization

Polymers DOZ and DOPh were obtained by the condensation reactions of 2,5-diformyl-3-dodecylthiophene with hydrazine and *p*-diaminobenzene, respectively. Elemental analysis and spectroscopic data suggest the molecular structures shown earlier. In particular, strong evidence for these structures is provided by the presence of the azomethine C=N stretching band at *ca.* 1590 cm⁻¹ (Fig. 1) and of the corresponding ¹H NMR peaks, between δ 8.5 and 9.0, both in the spectra of the two polymers and in those of the model compound DOA.

The length of the polymer backbone (n) depends on the reaction conditions. In particular, in the case of DOZ (Table 1), which was studied in more detail, the n value is affected by the solvent, the catalyst, the reaction time and the thermal curing. The water content of hydrazine does not produce



Fig. 1 FTIR spectrum of DOZ6, indicating the presence of the azomethine C=N stretching band (1598 cm⁻¹)

significant effects A satisfactorily high *n* value (and a low dispersion parameter, η) was obtained by adopting the conditions described for DOZ6 a light alcohol as solvent, the presence of a homogeneous protic acid catalyst and a suitable reaction time In the case of DOZ, the presence of the protic acid is crucial for the success of the preparation In fact, the reaction does not appear to begin until the trifluoroacetic acid is added, which produces immediately a colour change to dark red

The obtained material DOZ6 has an average molecular mass of 22×10^3 , corresponding to n=75 Conjugation is sufficiently extended to afford an electronic absorption maximum at 491 nm (Fig 2) No peaks attributable to terminal formyl groups were detected by IR (Fig 1) and ¹H NMR spectroscopies Probably the polymer chains are preferentially terminated by NH₂ groups whose peaks, however, have not been assigned equivocally in the spectra, owing to the probable presence of adventitious water in the spectroscopic samples

With regard to the effect of dry thermal curing on the fresh DOZ polyazines, Table 1 shows that it produces a significant increase in the molecular mass, but it also causes an unsatisfactory increase of the dispersity factor

The DOPh polymers were investigated to a lesser extent, owing to their lower solubility in the common organic solvents Nevertheless, the soluble fractions show rather satisfactory molecular masses and dispersities (Table 2) Note that in the case of DOPh the use of the acidic catalyst has the opposite effect with respect to DOZ, as its presence causes a lowering of the average molecular mass Furthermore, in the spectra of DOPh polymers the peaks attributable to terminal formyl groups (C=O stretch at *ca* 1660 cm⁻¹ and HCO proton



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resonance at δ ca 10) are very often detectable, mostly in the ¹H NMR spectra Their intensities depend on the *n* value, being low when *n* is high, as expected

The polymer containing the butylthiophene group (BUPh, Table 2) was synthesized under the same conditions as those used for DOPh2, in order to test the effect of the length of the side chain on the characteriscics of the polymeric azine. It appears that, with a longer lateral aliphatic chain, the growing polyazine becomes more soluble, resulting in a longer polymeric backbone of the soluble final product (DOPh2, n=62, BUPh, n=23)

Optical characterization

All optical investigations were performed on DOZ6 In Fig 3 the PBD spectrum of DOZ6 is shown The increasing absorption on the small wavelength side is due to the electronic absorption in the visible of the conjugated main chain ³ In the near-IR, clearly a variety of vibrational overtones can be found, which are due to the alkyl side chains The aromatic CH stretching vibration is too weak to be detected as overtones ¹⁹ The absorption coefficients (α_{el}) for the bands at 1064 and 1150 nm were taken from these data and are compared in Table 3 with the losses of the TE₀ modes of an unbleached slab waveguide

It is found for both wavelengths that more than 50% of the loss is due to scattering For higher waveguide modes (up to TE_4 and TM_4) the losses increase up to 15 dB cm⁻¹ (to the dominant loss feature) which indicates that surface scattering is an important problem The best spectral region, concerning the vibrational overtones and electronic absorptions, for using this material as a waveguide is at 1550 nm, one of the communication laser wavelengths, with an intrinsic absorption coefficient of 3 0 dB cm⁻¹, which is still too high for non-linear optical applications This is the lowest gap between two absorption bands of the overtones

Fig 4 shows a photograph of streaks taken at 1064 nm of the photobleached channel waveguide sample It can be seen clearly that the propagating wave is confined within the unbleached high index stripes (dark areas) The waveguide structures which can be seen are the exit ports of a pair of directional couplers The waveguide losses measured in these channel waveguides are of the same order of magnitude as the losses in the slab waveguide configuration Scattering contributions from the margin between the bleached and unbleached areas are minor

The sample was held so long in the mask aligner that the waveguide structures were bleached through and could be seen with the eye by the colour change to nearly transparent With



Fig. 3 PBD spectrum of DOZ6 The absorption bands marked with arrows are due to pure overtones of the stretching vibration of the order x (x, 0) and combination bands of stretching (x) and bending (y) vibrations (x, y) of the CH₃/CH₂ group

Table 3 PBD absorption coefficients compared with losses measured by waveguide attenuation at 1064 and 1150 nm. The difference of the waveguide attentuation and the PBD absorption yield the scattering losses in dB/cm.

		PBD		wavelength (TE_0)			
λ/nm	λ/nm	α_{ei}/cm^{-1}	$dB \text{ cm}^{-1}$	α_{tot}/cm^{-1}	dB cm ⁻¹	$\alpha_{\rm str}/{\rm dB}~{\rm cm}^{-1}$	
	1064	1.0	4.3	2.6	11.3	7.0	
	1150	1.05	4.6	2.4	10.2	5.6	
	1300	0.83	3.6				
	1550	0.69	3.0			_	



Fig. 4 Photograph of some channel waveguide streaks at 1064 nm. For better illustration the grey scale is inverted. The scattered light is represented by the dark areas. The laser is coupled with a prism at the right side of the image. The unbleached areas guide and confine the coupled light.

an *a* stepper (Tencor) the surface profile was scanned. It was found that the bleached regions decreased in thickness from 850 to 750 nm. Therefore the channel waveguide formation is not only due to the refractive index difference between the channel area and the bleached area, it is also due to an additional strip-loading effect.^{14,20-23} Therefore, it should be possible to fabricate channel waveguides also by brief bleaching.

The absorption coefficient difference, which occurs in parallel to the refractive index change during bleaching, is depicted in a 3D plot in the PBD image of the channel waveguides in Fig. 5 and as an absorption transmission spectrum in Fig. 6. The high stripes are the unbleached channel waveguides and the deep valleys are the bleached areas. Four y-junctions are depicted here. The sharp slopes of the channel waveguide margins show the good quality of the fabrication process. The



Fig. 5 PBD image of the channel waveguide sample taken at a pump wavelength of 532 nm.¹⁶ The image depicts a few y junctions: the high strips are the channel waveguides and the deep valleys are the bleached areas.



Fig. 6 Transmission absorption spectra of (a) unbleached and (b) bleached areas of the channel waveguide sample after 72 h of illumination in the mask-aligner

transmission absorption spectrum shows the disappearing of the electronic main absorption in the visible region from the conjugated main chain. The main chain and the conjugation are obviously destroyed by the bleaching process.

Conclusions

We have succeeded in preparing a new type of polymeric azine (DOZ), containing the 3-dodecylthiophene moiety, which is particularly suitable for the fabrication of channel waveguides. In spite of the intrinsic linear losses, still to high for $\chi^{(3)}$ non-linear optical applications, the spectral region of most use is one of the communication wavelengths. Other polyazines, with different substitution in the 3- and 4-thiophene positions will be prepared and tested.

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