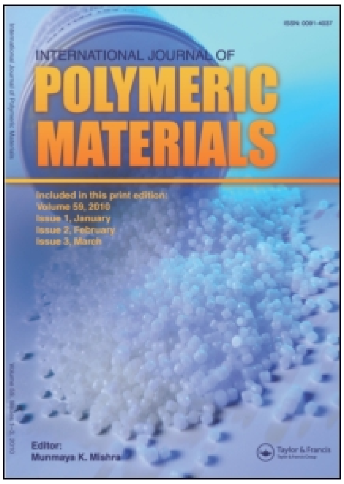

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Nonlinear Optical Behaviour of Polydiacetylene Coated Glass Waveguides

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Optical waveguiding in dielectric planar ion-exchanged glass waveguides coated with nonlinear polydiacetylenes is studied. Two polydiacetylenes were used in order to measure intensity–dependent guided waves, but a nonlinear optical response can only be seen for one, namely *p*-3BCMU. For the TM2–mode the real part of the third-order nonlinear susceptibility of *p*-3BCMU is determined to be $Re\chi^{(3)} = -3 \cdot 10^{-19}\,\mathrm{m}^2/\mathrm{V}^2$ at 1.064 μm using both shift in modenumber and nonlinear coupling.

Keywords: Glass waveguides; optical waveguiding; coatings; polydiacetylenes; nonlinear behaviour

1. INTRODUCTION

Devices based on nonlinear optical waveguiding are believed to be one way to obtain all-optical switching for optical communications and signal processing [1]. For two decades now, conjugated polymers, especially polydiacetylenes (PDAs), have been known to provide the relatively large off-resonant ultrafast nonlinearities required, and a significant body of research has been carried out in order to quantify and predict the origin and magnitude of their nonlinearity [2–5].

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*Corresponding author.

Not until rather recently however, has optical waveguiding in polydiacetylene films been reported, due to difficulties in purification and processing of these polymers [6, 7].

In this article, we describe the nonlinear optical behaviour of ion-exchanged glass waveguides coated with polydiacetylene films. Such a structure is commonly termed a four-layer structure as it consists conceptually of a glass substrate (refractive index n_s), a guiding ion-exchanged glass layer, a nonlinear polymeric cladding and an air superstrate (refractive index n_c). The reason for investigating this hybrid structure is that it is the easiest way to observe the polymeric nonlinearity in a waveguiding structure without using sophisticated deposition techniques. The obvious disadvantage is that the power in the polymer is only a fraction of the total guided wave power and thus the threshold power for the observation of nonlinear effects is relatively high, especially in comparison with the power required in a structure where the waveguide itself is the nonlinear medium. Bistability in a similar hybrid structure, consisting of a polydiacetylene film on a sputtered waveguide, has been observed [8].

The data analysis is based on the assumption that the nonlinearity only changes the guided wave modenumber, but not the field distributions (weak nonlinearities) [9–11]. This is justified by the numerical analysis of strong nonlinearities [12] that shows a guided power threshold of approximately 0.05–0.1 GW/cm for a system comparable to the one described. Taking 50 GW/cm^2 as an order of magnitude for the damage threshold of PDA, the value above is close to or even above the material's damage threshold.

2. THEORY

2.1. General Properties of the Four-layer Structure

General properties of the four-layer structure will be discussed firstly, *i.e.*, in particular the change in modenumber β/k and the fraction of the total guided power P that is in the polymer layer (P_{pol}/P) with varying polymer layer parameters (thickness d_{pol} and refractive index n_{pol}). As it is not easy to determine either refractive index or thickness of the polymer layer precisely, it is important to know how sensitive the waveguiding parameters are to changes in these quantities. Furthermore, the nonlinearity of the polymer manifests itself in a change in refractive index and thus the expected magnitude of the nonlinear effect can be estimated from these general properties.

The calculations were carried out with a multilayer-approximation of the graded-index profile, using a matrix-multiplication method [13]. For the index profiles a complementary error function was used in the case of K^+-exchange and a second-order polynomial for the Ag^+-exchange, as both profiles have been well-established in literature [14, 15] for the corresponding exchange.

The data was chosen so as to match the conditions of the experiments described below ($n_s = 1.504$, $n_c = 1.0$, $\lambda = 1064\,\text{nm}$, TM-modes). Care was also taken that the values of the polymer refractive index n_{pol} ranged between values smaller than the substrate index and larger than the surface index of the glass waveguides. The lower value can be justified in retrospect by the results, as the influence of the polymer layer is already weak at the lower value ($n_{\text{pol}} = 1.50$) and is even weaker for lower refractive indices.

Figures 1a and 1b illustrate the results and show the variation of the modenumber β/k as well as the fraction of power in the polymer layer with varying refractive index of the polymer layer for a 2nd order polynomial index profile. Two different thicknesses of 1 μm and 2 μm are compared and for the thinner layer the change in modenumber is small. The situation is different for high refractive indices or thick layers, as the polymer layer can then be regarded as a waveguide rather than an overlayer and is thus the mainly guiding layer.

The influence of a thin layer is only noticeable over a reasonably large refractive index range, which implies that nonlinear effects are not easily detected. Realistically a nonlinear induced refractive index change in a polymer is $\ll 0.01$, which would require a precision in β/k that is better than 10^{-5}. Only for $d_{\text{pol}} = 2.0\,\mu\text{m}$ do parts of the dispersion relation have a larger slope and it is interesting to note that the part of the dispersion curve where the slope increases, is not in the same refractive index range for different modes, but is at lower refractive indices for higher order modes. This means that a nonlinear effect can be better observed in one mode than in others, as the linear refractive index of the polymer is fixed and only a large slope of the dispersion curve ensures detectibility of the change in modenumber.

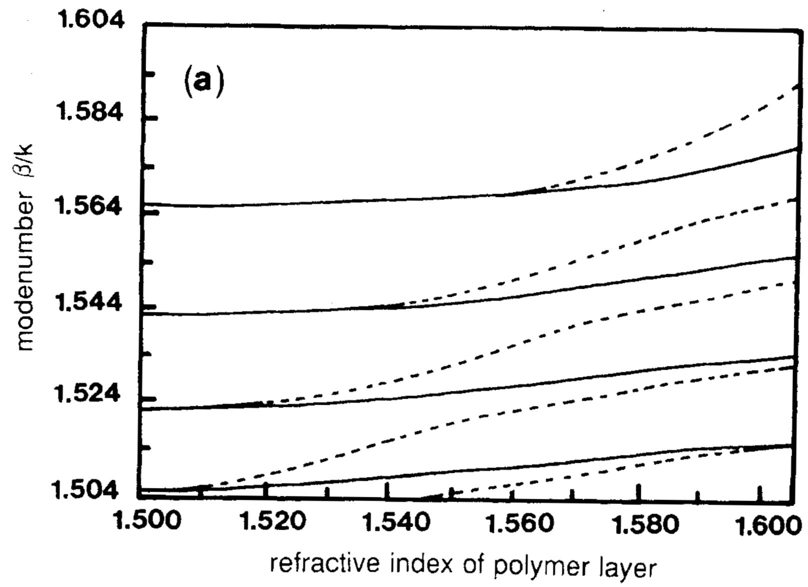


FIGURE 1a Variation of the modenumber β/k with refractive index of the polymer layer (2nd order polynomial). Dashed line: $d = 1\,\mu\text{m}$, full line: $d = 2\,\mu\text{m}$.

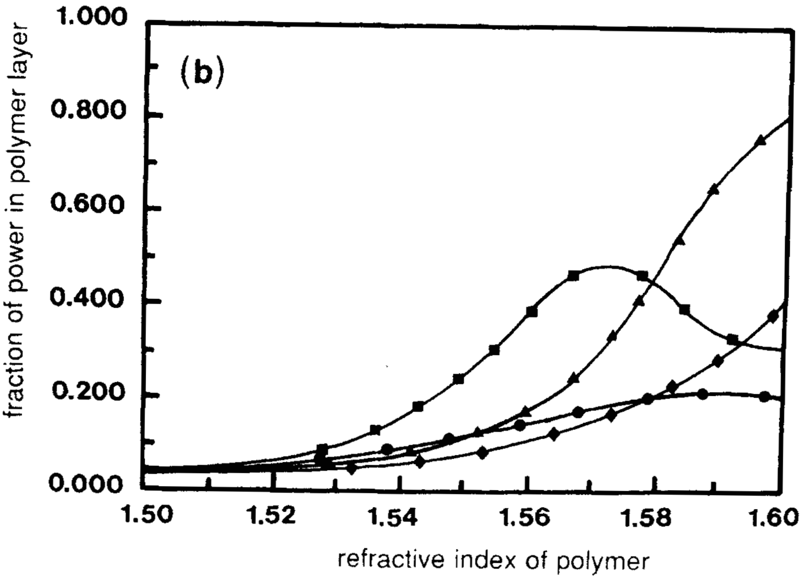


FIGURE 1b Variation of the power in the polymer layer with varying refractive index (2nd order polynomial). ◆: $d = 1\,\mu\text{m}$ (TM0); •: $d = 1\,\mu\text{m}$ (TM1); ▲: $d = 2\,\mu\text{m}$ (TM0); ■: $d = 2\,\mu\text{m}$ (TM1).

The corresponding power ratio is shown in Figure 1b and the most obvious characteristic is the appearance of a maximum for the TM1 curves, which can be observed for both thicknesses. For the TM0-modes the power will increase until it nearly reaches 100% (the mode is confined totally within the polymer layer), the same will eventually happen to the TM1-mode, *i.e.*, once the refractive index is high enough for the polymer layer to support also a first order mode, the mode will be confined to the polymer layer and most of the power will be in the polymer.

The results for a erfc-profile show similar behaviour. If the refractive index of the polymer layer is kept constant and the thickness is varied instead, the modenumber stays nearly constant for refractive indices considerably lower than the surface index of the glass waveguide, irrespective of the mode order. For high refractive indices additional modes can be supported by the waveguiding structure and thus the number of modes can serve as the first estimate of the polymer properties. The fraction of power in the polymer layer varies between 4–5% for low refractive indices and up to 60% for higher ones. However, these high percentages are only reached if the mode is mainly confined to the polymer.

In general, the power in the polymer layer is larger for a second order polynomial profile than for an erfc-profile. This can be explained by considering that for a second order polynomial profile the penetration of the waveguiding layer into the glass is not as deep as for an erfc-profile of comparable diffusion depth. Thus the same polymer layer thickness constitutes a larger perturbation to the system and in particular for small thicknesses the difference between the two index profiles is noticeable.

A problem that has to be considered here is the stability of the solutions obtained. This may be done by using the beam propagation method [16], and shows that the above approach is reasonable within experimental errors.

2.2. Nonlinear Waveguiding and Coupling

Third-order optical nonlinearities as observed in polydiacetylenes [5] manifest themselves in the simplest possible case as nonlinear refractive index changes $\Delta n = n_2 \cdot I$, where n_2 is the intensity-dependent refractive index and I the intensity. For an isotropic medium the nonlinear susceptibility $\chi^{(3)}$ is related to n_2 through

$$Re\chi^{(3)} = c\,\varepsilon_o n_o^2 n_2 \tag{1}$$

where n_2 has the same sign as $Re\chi^{(3)}$.

The effects of an intensity-dependent refractive index on the propagation parameters of the guided mode can either be calculated by assuming that the field distribution remains unchanged and only the modenumber β is intensity dependent ($\beta = \beta(I)$) or by solving Maxwell's equations including the nonlinear term from first principles.

Changes in field distribution require very high intensities as they only become significant when Δn is comparable to the difference of the linear refractive indices of *e.g.*, film and cladding. The intensities required to change only the modenumber β/k are much lower and the change in β ($\Delta\beta$) can be evaluated with the use of coupled-mode theory.

With the electric field written as $E_i(x, z) = f_i(x)\, b_i(z) \exp(-i\beta_m z)$, $f_i(x)$ being the field distribution and $b_i(z) = b_i(0) \exp(-i\Delta\beta P z)$, the change in modenumber can be expressed as [16]:

$$\Delta\beta P = \frac{c^2\varepsilon_o^2 k}{4}\int_{-\infty}^{+\infty} n_o^2 n_2 \left\{ \frac{2}{3}\cdot |f_i(x)|^2 \cdot |f_j(x)|^2 \cdot |b_j(o)|^2 + \frac{1}{3} f_i^{*2}(x)\cdot f_j^2(x)\cdot b_j^2(o)\cdot b_i^{*2}(o) \right\} dx \tag{2}$$

which can be simplified for TE-modes

$$\Delta\beta P = \frac{c^2\varepsilon_o^2 k}{4}\int_{-\infty}^{+\infty} n_o^2 n_2 |f_y(x)|^4 dx \tag{2a}$$

The $f_y(x)$ are normalised such that the $|b_y|^2$ are equivalent to the guided power in z-direction P.

The prism coupler, described in more detail *e.g.*, in Ref. [17], can also act as a nonlinear device [18–19]. For the input coupler (coupling angle Θ_p) the phase-matching condition ($\beta - kn_p \sin\theta_p = 0$) is not fulfilled for all intensities, as β is intensity-dependent and this will obviously influence the coupling efficiency. For an output coupler the phase-matching condition is always fulfilled and the effect of the nonlinearity only manifests itself in the intensity dependent phase shifts due to reflection at the boundary between linear and nonlinear medium [20]. This effect should be a lot smaller than the phase-mismatch. The coupling equation for a nonlinear material has been derived [21 – 22]

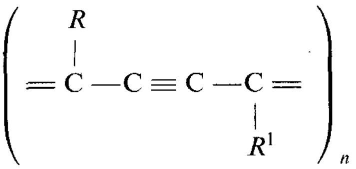
$$\frac{dA_g(z)}{dz} = t \cdot A_p(z) \cdot \exp(i(\beta - kn_p \sin \Theta_p)) - \left(\frac{\alpha}{2} + \frac{1}{L}\right) A_g(z) \qquad (3)$$

β is the nonlinear modenumber with $\beta = \beta m + \Delta\beta P$ (see [2]) and A_p the field amplitude at the base of the prism. t is a transfer parameter as defined in Ref. [17] and contains the coupling geometry. Solving the equation for constant coupling angle and varying power or constant power but varying coupling angle gives the theoretical coupling curves.

3. MATERIALS

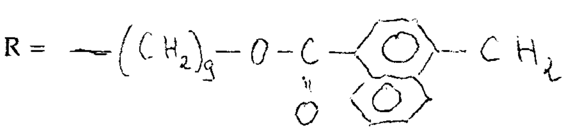
3.1. Polydiacetylenes

Two types of polydiacetylenes (PDAs) were used in this study, both chosen to have rather large side chains rendering them soluble in chlorinated organic solvents and thus solution processable. The chemical structural formula for PDA is



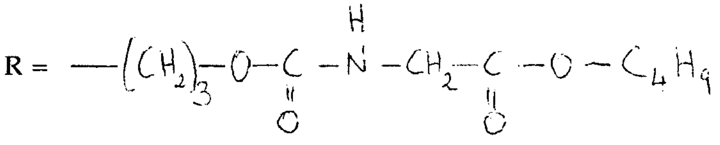
$$\left(= \overset{\overset{\displaystyle R}{|}}{C} - C \equiv C - \underset{\underset{\displaystyle R^1}{|}}{C} = \right)_n$$

with R, R^1 being the sidegroups. Both samples used have symmetric sidegroups ($R = R^1$). The ddd-2j monomer was synthesised as described by Plachetta *et al.* [24] with



Polymerisation was induced by UV– or γ–irradiation and the final product is a red polymer with a visible absorption spectrum as shown in Figure 2a for a 1 µm thick film.

The 3BCMU monomer was synthesised as described in [25] with a urethane based side group



$$R = -(CH_2)_3-O-\underset{\underset{O}{\|}}{C}-\overset{H}{N}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_4H_9$$

Polymerisation was induced by γ–irradiation giving a blue film with an absorption spectrum as shown in Figure 2b for 1.5 µm thickness.

The molecular weight of both polymers is in excess of $2 \cdot 10^5$ after purification.

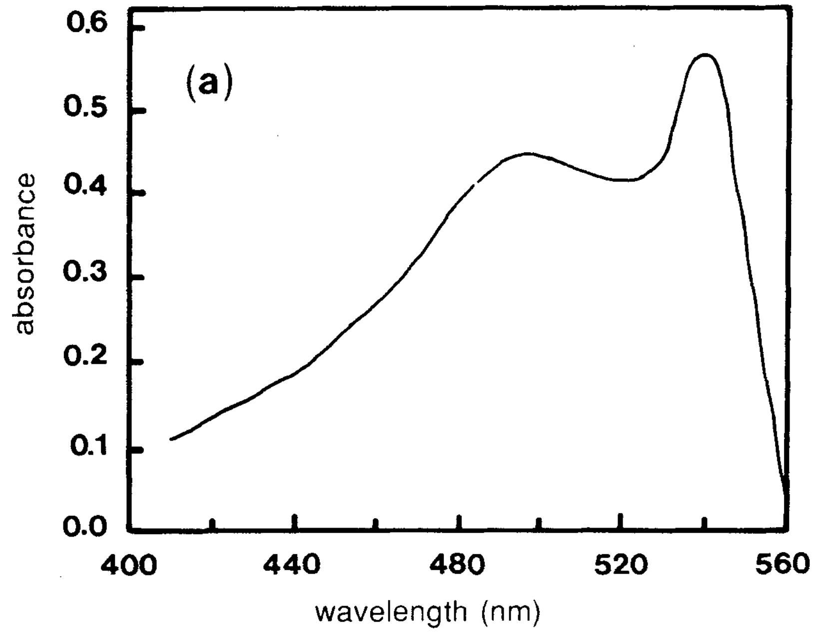


FIGURE 2a Visible spectrum for a *p*-ddd-2*j*-film (d = 1 µm).

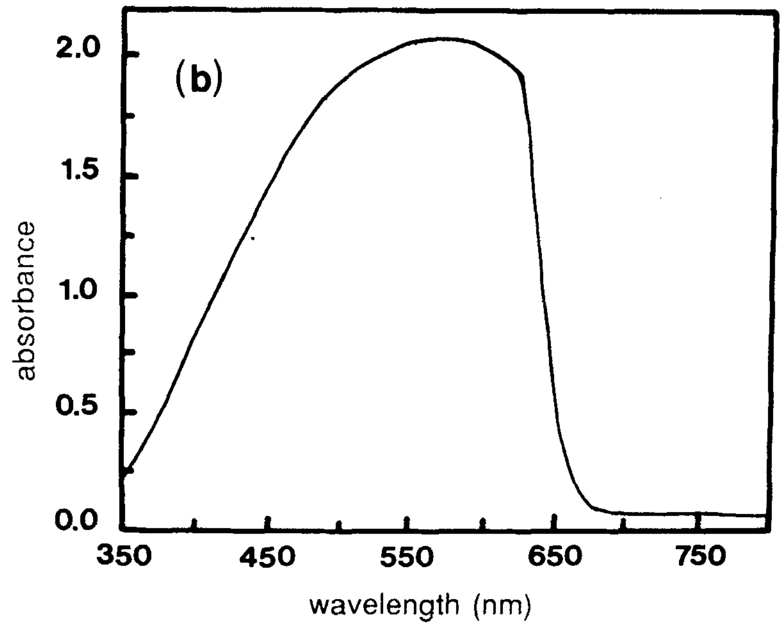


FIGURE 2b Visible spectrum for a *p*-3BCMU-film ($d = 1.5\,\mu m$).

Polymeric overlayers were formed on ion-exchanged glass waveguides by spin coating. Concentrations of 50 g/l were used with toluene and chloroform as solvent for *p*-ddd-2*j* and *p*-3BCMU, respectively. The thickness of the films was measured with a mechanical surface profiler and was found to be in the range of 1 μm for both films at spin speeds of 1000 rpm.

The edges of the films tend to be thicker than the rest of the film, therefore these were washed away to leave an approximately 2 cm long strip of polymer in the middle of the waveguide. In this way prism coupling could be used on the glass waveguide and the mechanical properties of the polymer need not be taken into account.

3.2. Properties of the Ion-exchanged Waveguides (Uncoated)

The first step in the experiment was the characterisation of the uncoated glass waveguides (one AG^+ exchanged and one K^+ exchanged waveguide). For this purpose the *m*-lines (bright lines) were recorded at three wavelengths: 532, 632.8 and 1064 nm and the refractive index change Δn and diffusion depth d were determined for each wavelength, the reason being that d does not change with wavelength and it is then possible to get a good fit for Δn.

The wavelengths 1064 and 532 nm were obtained from the fundamental and second-harmonic emission of a passively modelocked amplified Nd-YAG laser emitting single pulses of 50 ps duration and 3 Hz rep. rate.

For all measurements the data at 632.8 nm (HeNe laser) had the highest precision and therefore the value of d obtained with this data was assumed to be closest to the real value. The largest error normally arises from the measurement of the zero point, being larger at 1064 nm than in the visible.

The K^+-exchanged waveguide supported 4 modes at 532 nm, 3 modes at 632.8 nm and 2 modes at 1064 nm. The Ag^+-exchanged waveguide supported 7 modes at 532 nm, 6 modes at 632.8 nm and 3 modes at 1064 nm. The value for the angle corresponding to each mode was obtained as an average of several measurements and the standard deviation was taken as the mean error of the experiment. If the error in coupling angle is $\delta\alpha$, the resulting error in modenumber β/k can be derived from

$$\delta(\beta/k) = \frac{d(\beta/k)}{d\alpha}\delta\alpha$$

For the calculation of the theoretical modenumbers the multilayer method was used [13], as it is the only method that allows inclusion of the polymeric overlayer without difficulties. The disadvantage is that quite a large number of layers is necessary to get a good fit, which in turn increases the required computing time. Therefore a compromise between precision and computing time has to be made, depending on the requirements of the experiment. An approximation of 100 layers was found to be sufficient in this case. It should be noted that an approximation with too few layers can give the wrong number of modes that are supported by the waveguide.

Table I shows experimental and theoretical results for the modenumber β/k, where the theoretical modenumbers correspond to the values of Δn and d for which the lowest deviation σ (see [28]) was obtained.

TABLE I Comparison of experimental and theoretical mode numbers of the ion-exchanged waveguides

$K^{\pm}$-exchange

	$\lambda = 532\,nm$		$\lambda = 632.8\,nm$		$\lambda = 1064\,nm$	
	$\beta/k\,(exp.)$	$\beta/k\,(theor.)$	$\beta/k\,(exp.)$	$\beta/k\,(theor.)$	$\beta/k\,(exp.)$	$\beta/k\,(theor.)$
TE0	1.5233	1.52191	1.5184	1.51770		
TE1	1.5214	1.51893	1.5157	1.51469		
TE2	1.5198	1.51688	1.5134	1.51283		
TE3	1.5159	1.51555				
TM0			1.5110	1.51762	1.5095	1.50795
TM1			1.5166	1.51463	1.5061	1.50459
TM2			1.5141	1.51279		

Ag^{+}-exchange

	$\lambda = 532\,nm$		$\lambda = 632.8\,nm$		$\lambda = 1064\,nm$	
	$\beta/k\,(exp.)$	$\beta/k\,(theor.)$	$\beta/k\,(exp.)$	$\beta/k\,(theor.)$	$\beta/k\,(exp.)$	$\beta/k\,(theor.)$
TE0	1.5849	1.58854	1.5792	1.58123		
TE1	1.5719	1.57404	1.5633	1.56498		
TE2	1.5607	1.56140	1.5492	1.55072		
TE3	1.5500	1.54968	1.5350	1.53746		
TE4	1.5396	1.53853	1.5218	1.52483		
TE5	1.5286	1.52779	1.5113	1.51339		
TE6	1.5189	1.51772				
TM0					1.5613	1.56301
TM1					1.5419	1.53906
TM2					1.5184	1.51786

For the substrate index, normal dispersion for soda-lime glass was assumed ($n(523\,\text{nm}) = 1.515$, $n(632.8\,\text{nm}) = 1.512$, $n(1064\,\text{nm}) = 1.504$). As the soda-lime glass that is used for the substrates (microscope slides) is not a highly defined glass in terms of optical properties these refractive indices are not high precision values.

The error in modenumber $\delta\,(\beta/k)$ was evaluated to be $3 \cdot 10^{-4}$ in the visible and $\approx 10^{-3}$ for $\lambda = 1064\,\text{nm}$ for the experimental data. The theoretical β/k are precise to the last given decimal within the used 100-layer approximation. The discrepancy between theoretical and experimental values is due to assumptions such as the index profile, the substrate index or the 100-layer approximation which are not strictly valid in this case.

To obtain the best values for Δn and d, several pairs of $(\Delta n, d)$ were evaluated with the corresponding σ. The value for d was increased in steps of 0.25 μm, Δn was changed in steps of 10^{-3} (K^+-exchange) or $2.5 \cdot 10^{-3}$ (Ag^+-exchange).

(a) Ag^+-exchange: $d = 7.0\,\mu m$

$$\begin{aligned}\Delta n(532\,\mathrm{nm}) &= 0.0905\\ \Delta n(632.8\,\mathrm{nm}) &= 0.0875\\ \Delta n(1064\,\mathrm{nm}) &= 0.0850\end{aligned}$$

(b) K^+-exchange: $d = 7.25\,\mu m$

$$\begin{aligned}\Delta n(532\,\mathrm{nm}) &= 0.011\\ \Delta n(632.8\,\mathrm{nm}) &= 0.010\\ \Delta n(1064\,\mathrm{nm}) &= 0.010\end{aligned}$$

These values are in good agreement with published data for similar fabrication conditions [14, 15]. Birefringence in the case of K^+-exchange was not found. In order to check the quality of the calculations the diffusion depth d was also calculated for the Ag^+-exchange using the WKB-approximation (see [27], introducing a dimensionless parameter $\tilde{x} = x/d$), the diffusion depth d can be evaluated as

$$d = (m + 3/4)\pi/k \Big/ \int_0^{\tilde{x}_t} \{n^2(\tilde{x}) - (\beta/k)^2\}^{1/2} d\tilde{x}$$

The phase ϕf_c has been taken as $\pi/2$ for simplicity. This gave the value of $d = (7.1 \pm 0.4)\,\mu m$ and thus confirmed the value of d within error.

The attenuation for the waveguides was 2 dB/cm for the Ag^+-exchanged waveguide and 1dB/cm for the K^+-exchanged waveguide.

4. THE FOUR-LAYER STRUCTURE

4.1. Linear Optical Properties of the Coated Waveguides

To study the properties of the PDA *p*-ddd-2*j*, a film was spun onto a K^+-exchanged waveguide. The K^+-exchanged waveguide was chosen, because the polymer has a refractive index of approximately 1.5 and the surface index of the K^+-exchanged guide matches this value better than that of the Ag^+-exchanged guide. The linear characterisation was carried out first. For this purpose the modenumbers of the coated waveguide were measured using a prism coupler and the optimum coupling angle was determined. The values that were obtained for the modenumbers ($\beta/k(\mathrm{TM0}) = 1.51069$, $\beta/k(\mathrm{TM1}) = 1.50658$) were compared with the theoretical results of the multilayer approximation and the best values for refractive index and thickness of the polymer film were found to be $d_{\mathrm{pol}} = 1.2\,\mu\mathrm{m}$ and $n_{\mathrm{pol}} = 1.508$. The thickness is in good agreement with the mechanical step measurement and the refractive index seems also reasonable, however, as the variation of β/k with n_{pol} is small in the refractive index region considered, the error in n_{pol} is approximately $5 \cdot 10^{-3}$.

The polymer *p*-3BCMU has been used in waveguiding experiments as a waveguiding material [6, 7, 35, 36] and its refractive index for TM-modes was found to be $n_{\mathrm{pol}} = 1.585$. This value is very close to the surface index of a Ag^+-exchanged waveguide, which is 1.589, and considering the theoretical results of the multilayer approximation that show a large dependence on polymer properties for a 2nd order polynomial profile, it seemed to be a promising combination. Again the linear characterisation was carried out first. A set-up employing a second prism was used to couple out the light. The outcoupled *m*-lines correspond to the modenumbers that are supported by the structure at the outcoupling prism, *i.e.*, the edge of the outcoupling prism has to be on the polymer for the properties of the four-layer-structure to be seen. The evaluation of the modenumbers from the input angels showed three modes ($\beta/k(\mathrm{TM0}) = 1.5623$, $\beta/k(\mathrm{TM1}) = 1.5406$, β/k $(\mathrm{TM2}) = 1.5198$), which does not agree well with the theoretical data for $n_{\mathrm{pol}} = 1.585$ and $d_{\mathrm{pol}} = 1.0\,\mu\mathrm{m}$. This can be explained by the thickness variation of the film, which tends to form anisotropic structures as observed by SEM.

The thickness of $1\,\mu\mathrm{m}$ that has been measured by the mechanical surface profiler corresponds to a thicker part of the film and the layer under the outcoupling prism was thinner, additionally compressed by the pressure applied between prism and waveguide. By comparing the theoretical results from Section 2 with the experimentally obtained modenumbers, the thickness of the polymer below the prism was determined to be $(0.3 \pm 0.1)\,\mu$m. Also considered should be that the determination of the modenumbers was not carried out at low intensities, because detection at low intensities was difficult and thus, not the linear refractive index of 1.585, but a lower (intensity-dependent) refractive index should in principle be taken to evaluate the theoretical modenumbers.

4.2. Attenuation

For PDA *p*-ddd-2*j* samples, the attenuation was determined by measuring the scattered signal along the guided track over a distance of 1 cm in 0.5 mm steps and was found to be 4 dB/cm. Neglecting the attenuation due to surface scattering ($\alpha_{SS} = 0$) and assuming a weakly guiding system, *i.e.*, $n_S + \Delta n$ is of the same order of magnitude as n_{pol}, the total attenuation can be written as [28]

$$\alpha_{\text{tot}} = \alpha_{\text{pol}} \cdot P_{\text{pol}}/P + \alpha_{\text{K}^+} \cdot P_{\text{glass}}/P \tag{5}$$

with α_{tot}: total attenuation; α_{pol}: volume loss in the polymer layer; α_{K^+}: volume loss in the glass waveguide; P_{pol}/P: fraction of power in the polymer layer, P_{glass}/P: fraction of power in the glass guide.

For α_{K^+} a value of 1 dB/cm was taken and this leads to an estimate of $\alpha_{\text{pol}} \approx 92$ dB/cm. Comparing this value to the value of 100 dB/cm that has been measured in Langmuir–Blodgett films and in the polydiacetylene PTS [29] and taking the poor fabrication (no clean room) conditions into account, this seems to be a reasonable result [35]. Improved fabrication conditions should reduce it considerably.

PDA *p*-3BCMU, on the other hand, has been shown to form low-loss, high quality wave guides. Hence, the attenuation was measured for two modes and determined to be 2.4 dB/cm (TM0-mode) and 3.1 dB/cm (TM2-mode). Taking the powers in the polymer layer this difference can only be explained if surface scattering is considered, volume loss alone cannot account for it. The simple approximation (5) cannot be used, as the glass-polymer interface plays an important part in the overall attenuation. An overall attenuation as a sum of volume loss and surface scattering follows as

$$\alpha_{\text{tot}} = \alpha_{\text{pol}} \cdot P_{\text{pol}}/P + \alpha_{K^+} \cdot P_{\text{glass}}/P + C \cdot \{1 - (\beta/kn)\}^{3/2}/(\beta/kn) \tag{6}$$

and eliminating the constant C from the values obtained for the two modes, a volume loss of approximately $\alpha_{\mathrm{pol}} \approx 5\,\mathrm{dB/cm}$ can be estimated, in agreement with previously reported values.

4.3. Nonlinear Optical Characterisation

4.3.1. Nonlinear Attenuation

In order to assess the nonlinear properties of the material, several techniques were used. The first option was to look at the change in radiated light along the streak, *i.e.*, the attenuation, with intensity. If the approximate formula (5) is valid, then even a small change in P_{pol} will influence the total attenuation. Using the data from Section 2.1 and the value of 4 dB/cm for low intensities, an estimate for the change in attenuation can be made. Assuming a nonlinearity of $\chi^{(3)} = 6 \cdot 10^{-19}\,\mathrm{m}^2/\mathrm{V}^2$ that has been reported for PTS-films [3], a refractive index change of $3 \cdot 10^{-3}$ seems feasible. Depending on the sign of nonlinearity the resulting refractive index is either $n_{\mathrm{pol}} = 1.505$ or $n_{\mathrm{pol}} = 1.511$. The fraction of power in the polymer layer is then $P_{\mathrm{pol}}/P = 4.1 \cdot 10^{-2}$ ($n_{\mathrm{pol}} = 1.511$) and $2.8 \cdot 10^{-2}$ ($n_{\mathrm{pol}} = 1.505$) (from Section 2.1). The corresponding attenuations are 3.3 dB/cm and 4.7 dB/cm, values that should be easily detectable.

Endfire coupling was used for these measurements, as it is easy to block the light that is scattered at the edge of the waveguide (blocking the light that is scattered at the edge of the prism in the case of a prism coupler is more difficult). Also measurements can be taken on the uncoated part of the sample, which can serve as a reference, as no nonlinearity should be seen there.

The problem of precise reproducibility of the fibre position influences the measured value of the attenuation and thus the radiation as a function of intensity was measured while the fibre was kept at one position. Thus the measured property was not α as defined in (5) but log $(P_{\mathrm{scatt}}/P_{\mathrm{input}})$, *i.e.*, the measured property is not normalised with length. The result is shown in Figure 3, where log $(P_{\mathrm{scatt}}/P_{\mathrm{input}})$, is plotted against guided wave power (value is corrected for coupling efficiency), for both a point on the polymer layer and for a point on the uncoated waveguide. There is no qualitative difference between the two curves, *i.e.*, in both cases log $(P_{\mathrm{scatt}}/P_{\mathrm{input}})$ is independent of intensity and thus no nonlinear effect could be seen.

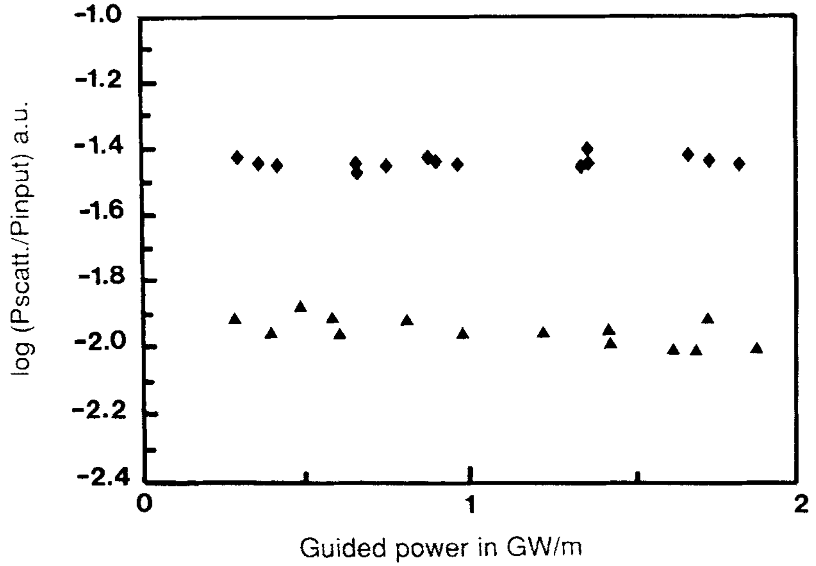


FIGURE 3 Variation of the scattered signal from coated and uncoated part of the sample with intensity; ▲ signal from polymer coated sample; ◆ signal from uncoated sample.

Two reasons could be responsible: either the dispersion curve (Fig. 1a) is too flat, *i.e.*, the change in P_{pol}/P with refractive index is too small, or a large part of the attenuation is due to surface scattering. An estimation of the dependence of the surface scattering on the intensity can be made using [28]

$$\alpha_{\mathrm{SS}} = C \cdot \{1 - (\beta/kn)\}^{3/2}/(\beta/kn) \qquad (7)$$

where C is a constant that can be determined from experiments and n is the highest refractive index in the four-layer structure. Using the same index change of $3 \cdot 10^{-3}$ as in the volume loss estimation and determining C with the value of α for low intensities, the surface scattering is evaluated as (assuming that half of the total loss is due to surface scattering) $\alpha_{SS} = 2.025\,\mathrm{dB/cm}$ ($n_{\mathrm{pol}} = 1.505$) and $\alpha_{SS} = 1.97\,\mathrm{dB/cm}$ ($n_{\mathrm{pol}} = 1.511$) compared to 2.0 dB/cm for the low intensity measurement. This is a small variation with intensity which would be difficult to detect against noise background. As the signal that is detected by the fibre is small, the noise background limits the detectibility of nonlinear effects. Another problem connected with the estimate of the change in volume loss is that the calculation is based on the assumption of a homogenous refractive index change throughout the polymer layer. Equation (2) shows that one has to average over the field distributions to calculate the change in modenumber $\Delta\beta P$ and this usually leads to a smaller change in β than if just an intensity-dependent refractive index, homogeneous throughout the polymer layer, is assumed.

A further simplification made in the calculations is that no attenuation was considered. Including the attenuation will change the results, as the guided wave power will then be dependent on the length of the guided streak, reducing the precision of the measurement of nonlinear properties substantially.

4.3.2. Shift in Mode-number

A simple way to observe the nonlinearity of the polymer cladding is by measuring the coupling angle as a function of intensity in a prism coupler which is equivalent to finding the variation of β/k with intensity. The mode was first optimised by eye and then an angular range of 0.24° was scanned in steps of 0.02°, while the output intensity was focused onto a photodiode. The pulse length of the Nd:YAG laser used was 50 ps and the beam was focussed down to a spot size of 500 μm diameter in the coupling region.

A Gaussian curve was fitted to each of the angular scans and then maximum and half width of each curve were determined from the fits. The variation of the angular maximum with guided wave power is shown in Figure 4 for *p*-ddd-2*j*. The arrows indicate the temporal order of the measurements. It can be seen that the angle decreases the longer the measurement proceeds, but shows no other simple variation with intensity. This indicates a change in material properties, taking place during the measurement. The half widths of the curves show no dependence on intensity.

As each measurement takes a considerable amount of time (a scan at one intensity consists of 12 angle positions with averaging 40 pulses each time), the process that leads to the change in material properties

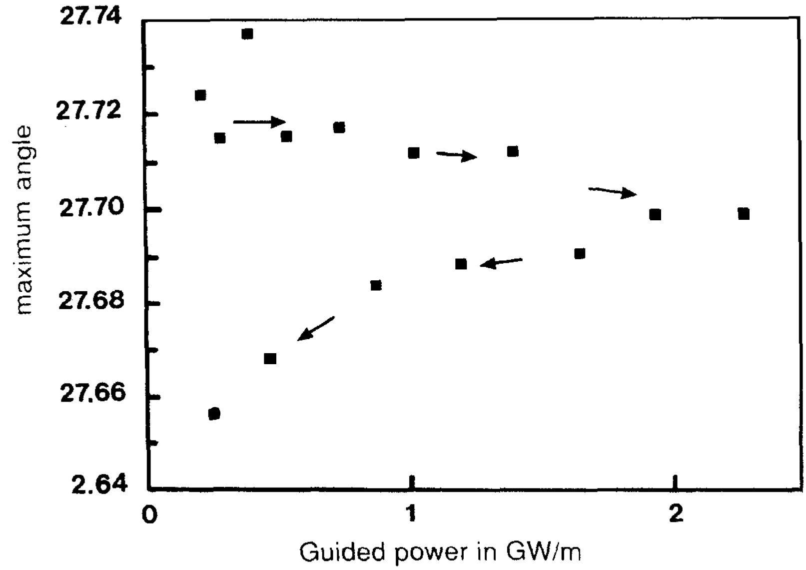


FIGURE 4 Variation of optimum coupling angle with intensity for PDA *p*-ddd-2*j*.

is either a slow process or permanent damage is done at each shot. If it is permanent damage, then the threshold for the process seems to decrease, once the damage has started, as the decreasing trend in Figure 4 continues down to lowest powers (< 0.5 GW/m), but the first onset seems to be only for powers larger than 1 GW/m.

A decrease in refractive index during exposure to a laser beam has been observed in the polydiacetylene *p*-4BCMU, when exposed to light tuned within the absorption band of the polymer [30]. The absorption of *p*-ddd-2*j* has its maximum around 530 nm (red form of PDA) and thus a two-photon-resonance will lead to a similar effect. However, as removal of the polymer cannot be excluded, it is also possible that absorption at impurities and subsequent heating (the polymer has a melting point of 47°C, [24]) are responsible for the decrease in coupling angle.

For the observation of nonlinear effects in a four-layer-structure with a polymer layer, the combination of *p*-ddd-2*j* with a K^+-exchanged waveguide does therefore not seem to be promising, both from the properties of the polymer and from theoretical considerations of an erfc-profile type waveguide.

Thus the other structure consisting of a Ag^+-exchanged waveguide with a *p*-3BCMU film was investigated. Again the output intensity as a function of angular position and intensity was measured. This time for the TM0-mode a reversible shift of 0.02° between low and high intensity optimum coupling angle has been observed (see Fig. 5). This angular shift can be converted into a shift in modenumber using (3) and for an angle $\alpha' = \alpha + \delta\alpha$ ($\delta\alpha \ll 1$), this shift is

$$\Delta(\beta/k) = \delta\alpha \cos\alpha \left(\cos\varepsilon - \sin\varepsilon \frac{\sin\alpha}{\sqrt{n_p^2 - sin_\alpha^2}} \right) \qquad (8)$$

To simplify calculations, Eq. (2a) was used for the evaluation of nonlinearities, although it is valid for TE-modes and the measurements were done with TM-polarised light. However, this should not

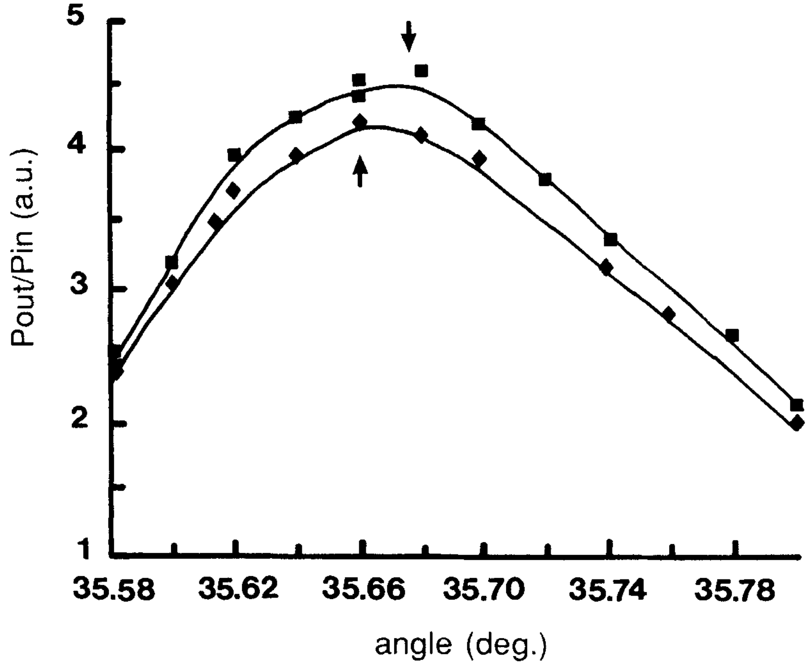


FIGURE 5 Shift of *m*-line and thus β with intensity in *p*-3BCMU, upper curve is for lower intensity (0.2 GW/M) and lower curve for higher intensity (0.5 GW/m). Measurements below 0.2 GW/m show no difference to the upper curve.

result in error in the nonlinearity that is larger than the experimental error.

Using (2a) the nonlinearity n_2 can be evaluated and this leads to $n_2 = -(4 \pm 2)\ 10^{-17}\,\mathrm{m}^2/\mathrm{W}$ or $Re\chi^{(3)} = -(3 \pm 1.5) \cdot 10^{-19}\,\mathrm{m}^2/\mathrm{V}^2$. (The guided wave power was corrected for the coupling efficiency). This nonlinearity agrees with solution measurements [31] and is also within a factor of 3 of the value of $\chi^{(3)}$ in a blue polydiacetylene film, determined by 3rd harmonic generation [2, 4]. The negative sign is in agreement with the solution data.

In this case, damage as a reason for the shift can be excluded, as all measurements were performed by starting at medium intensities, then increasing the intensity, decreasing and increasing it again until the original value was obtained. As the output values for the same input intensities coincided within experimental error, a permanent change in material properties was eliminated.

4.3.3. Nonlinear Coupling

Another effect that could be observed with the *p*-3BCMU structure was that of nonlinear coupling. This is possible, if the coupling prism is not placed on an uncoated part of the sample, but some polymer is between prism and glass. The throughput as a function of intensity and angle was determined for the TM2-mode, both for coated and uncoated samples. For two fixed angular positions it is shown in Figure 6a for a coated sample and in Figure 6b for an uncoated one. The maximum value of 2.8 in Figure 6a corresponds to a throughput of $P_{\mathrm{out}}/P_{\mathrm{in}} = 0.035$, which, after the power loss due to attenuation has been accounted for, is equivalent to a coupling efficiency of 35%. The maximum of 1.0 in Figure 6b corresponds to a coupling efficiency of 30%.

As an intensity-dependence can only be seen for the coated sample, the nonlinear effect is due to the polymeric nonlinearity. The measured quantity is the output power divided by the input power, $P_{\mathrm{out}}/P_{\mathrm{in}}$, which can be written as:

$$P_{\mathrm{out}}/P_{\mathrm{in}} = \eta_{\mathrm{in}} e^{-\alpha l} \eta_{\mathrm{out}} \tag{9}$$

where η_{in} is the input coupling efficiency; $e^{-\alpha l}$ is the power loss due to attenuation in the waveguide and η_{out} the output coupling efficiency.

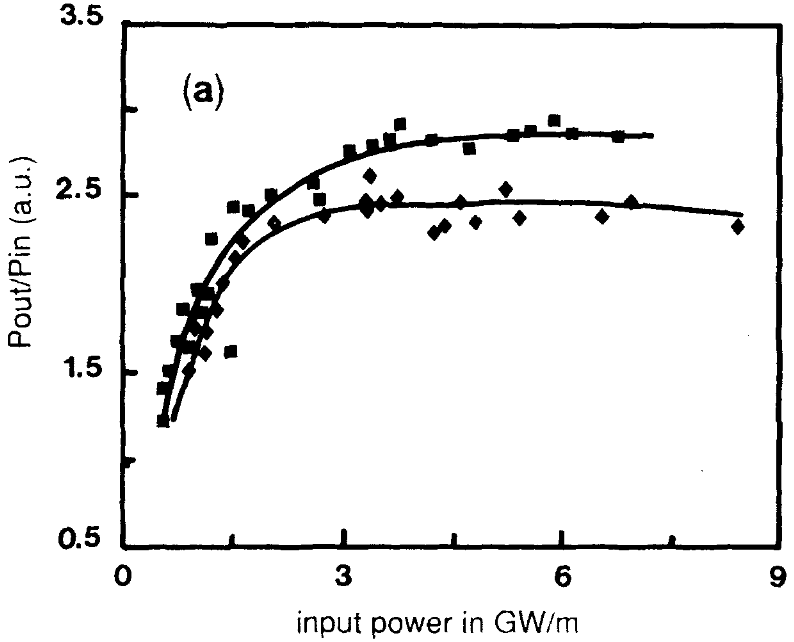


FIGURE 6a Ratio of output and input power as a function of input power (TM2-mode), upper curve corresponds to the detuning for optimization at $3 \cdot 10^9$ W/m, lower curve is 0.02^0 detuned from this value.

Although the output efficiency has been predicted to show intensity-dependent behaviour [20], this effect is not very strong (the phase-matching condition is automatically fulfilled). The attenuation coefficient, and thus the power loss, was not found to be strongly intensity-dependent in the scattering experiments, and although the noise level was quite high, no significant contribution is expected from that term. Several experimental and theoretical investigations have shown that the input coupling efficiency depends on the input power [19, 32–34]. However, comparing the experimental results shown in Figure 6(a) to the commonly published theoretical predictions, it is noticeable that the coupling efficiency decreases with increasing power for the published curves, but the experimental data in Figure 6a shows an increasing coupling efficiency with increasing power. The reason for this difference is the different optimisation conditions. Most publications assume that the prism coupler is optimised for low intensities, *i.e.*, the linear case. The optimisation for the data in Figure 6a was

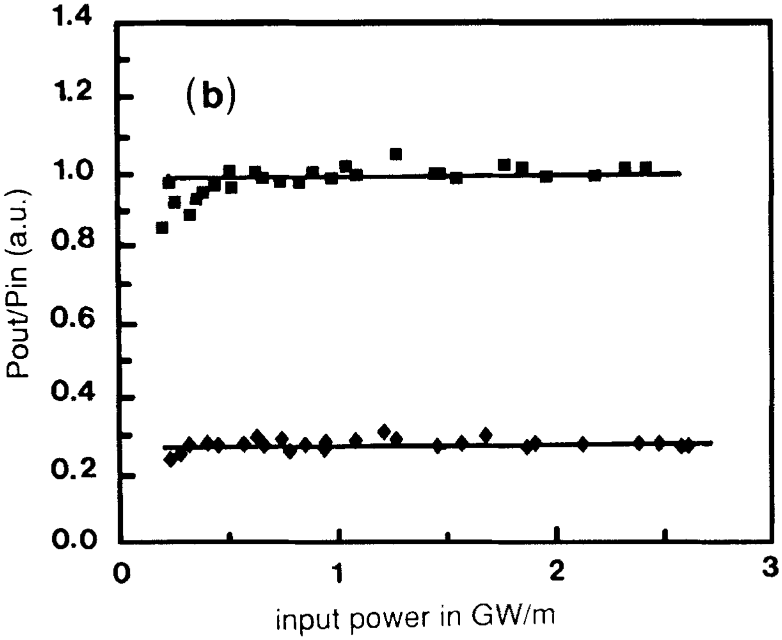


FIGURE 6b Uncoated sample as a comparison to Figure 6a (TM2-mode), upper curve corresponds to an angle at the maximum of the *m*-line, the lower one is detuned by 0.06^0.

carried out at a power of $3 \cdot 10^9$ W/m, a value that is large enough to see a nonlinear effect.

Optimisation means that the phase-mismatch $(\beta_m + \Delta\beta P - kn_p \sin\theta)$ equals zero. Introducing the dimensionless detuning parameter $\Delta N = (n_p k \sin\theta - \beta_m)2\,W_0$, the phase-mismatch can be written as $\Delta\beta P - \Delta N/(2\,W_0)$. Optimisation in the linear case is equivalent to an initial detuning $\Delta N = 0$, whereas at an arbitrary power level corresponds to an initial detuning of $\Delta N = 2\,W_0 \Delta\beta P$. Equation (3) was integrated numerically and curves for several detunings have been evaluated (see Fig. 7). The linear coupling efficiency is not as high as the optimum value of 0.8, but this is due to the fact that for the reradiation length l and the termination of the prism x_S the values that have been optimised for a step-index guide ($1/W = 1.48$, $X_S/W = 0.76$) were used. The experiments were done with a graded-index guide, and the modenumbers as well as the averaging integral were evaluated with data from the multilayer approximation.

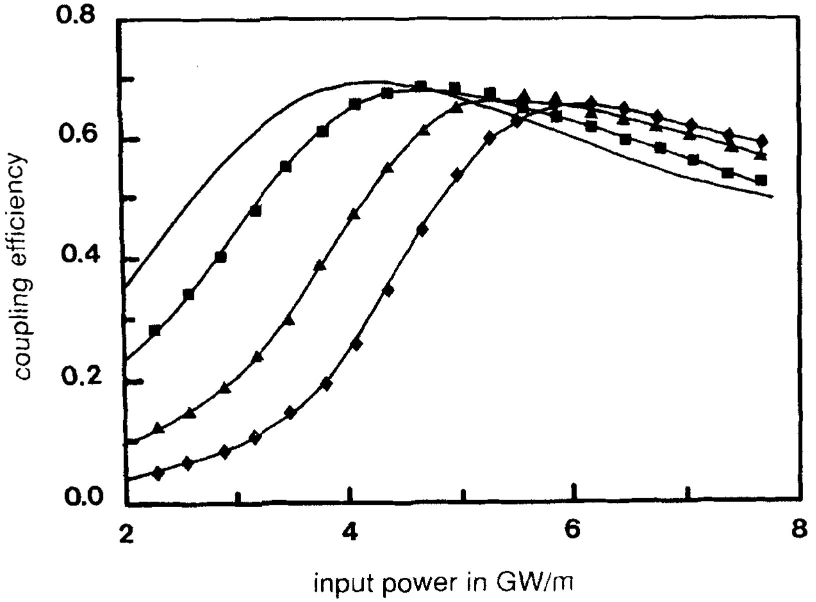


FIGURE 7 Numerical results for several detunings ($N = -3.0$ (–) $\Delta N = -3.2$ (■), $\Delta N = -3.5$ (▲) and $\Delta N = -3.7$ (◆)). The scale on the x-axis is linear to allow comparison with the experimental data in Figure 6(a).

It is easily seen that for a high enough detuning the behaviour is similar to the one that has been observed. The behaviour that has been reported by Assanto *et al.* [33] appears to be similar, but their detuning was five times the original linewidth, whereas the detuning used for Figure 7a was less than a linewidth.

Figures 8a and 8b show the coupling efficiency *versus* detuning curves at three different intensities for both coated and uncoated sample. These curves should be compared with the results presented in Ref. [22] because the sign of the nonlinearity is negative in Figure 8(a) but positive in Ref. [22].

The theoretical curves were adjusted until they fitted the experimental data as closely as possible and the nonlinearity was determined to be

$$n_2 = -(5 \pm 3)\,10^{-17}\mathrm{m}^2/\mathrm{W} \quad \text{or} \quad Re\,\chi^{(3)} = -(3.8 \pm 2.2)\,10^{-19}\mathrm{m}^2/\mathrm{V}^2$$

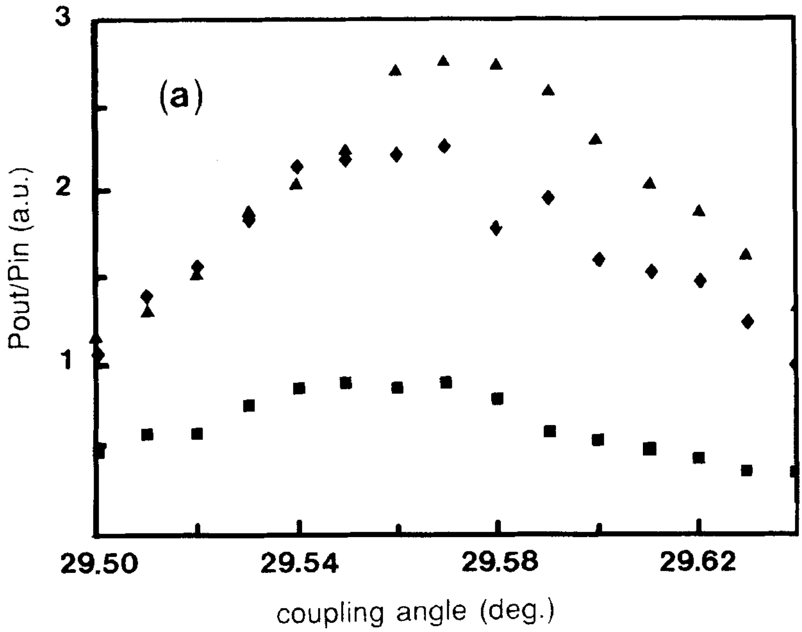


FIGURE 8a Coupling efficiency *versus* detuning curve for the coated sample (power levels are $4.5 \cdot 10^9$ W/m (▲), $2.7 \cdot 10^9$ W/m (◆) and $2.5 \cdot 10^8$ W/m (■)).

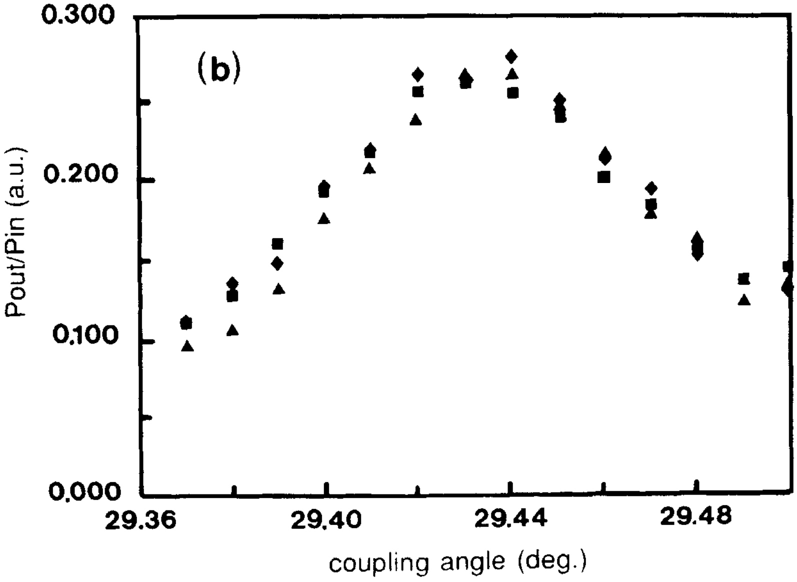


FIGURE 8b Coupling efficiency *versus* detuning curve for the uncoated sample (power levels are $2.5 \cdot 10^9$ W/m (▲), $7.5 \cdot 10^8$ W/m (◆) and $2.5 \cdot 10^8$ W/m (■)).

The calculations were done for an ideal Kerr-like material as typical for an electronic nonlinearity and no thermal contribution was taken into account. This can be justified by the calculations of Stegeman *et al.* [23] who showed that for pulsed excitation with material parameters typical for polydiacetylenes, the thermal contribution to prism coupling is negligible for pulse widths substantially less than a nanosecond. Also the response time of the material is fast compared to the pulse width, which is equivalent to using the theory for cw excitation.

5. CONCLUSIONS

The four-layer structure offers the advantage that coupling problems that might occur with polymer waveguides do not exist. This makes it interesting for both commercially oriented investigations in optical switching devices, where high coupling efficiencies are important, and basic research, where the material might be unsuitable for forming a waveguide.

The theoretical calculations show that it is favourable to choose the surface index of the glass waveguide and refractive index of the polymer as close together as possible. As most polymer films have a comparatively high attenuation, either the refractive index of the polymer should be lower than the surface index of the waveguide or the film has to be thin in order to keep the overall attenuation low.

Intensity-dependent attenuation/scattering measurements did not show any result, however, measurements with a reduced noise background might be able to resolve such an intensity-dependence.

The experiments with the polydiacetylene *p*-ddd-2j show that even with the four-layer-structure not all polydiacetylenes are equally suitable for waveguiding experiments. The change in refractive index, however, deserves to be looked at more closely to understand which process is responsible.

The nonlinearity of the polydiacetylene *p*-3BCMU was investigated quantitatively using both a shift in modenumber and nonlinear coupling and a nonlinearity of $Re\,\chi^{(3)} = -3 \cdot 10^{-19}\,\mathrm{m}^2/\mathrm{V}^2$ was found in both measurements. This value agrees well with other publications.

Thus the four-layer structure is an attractive way of both determining and using a polymeric nonlinearity, if either material or deposition technique is not suitable to form a good waveguide.

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