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Thermally stable cross-linked polymers for electro-optic applications

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Abstract. — The electro-optic properties of a new variety of cross-linked polymer referred to as Red-acid Magly are being reported. Its linear and nonlinear optical properties are characterized in comparison with the classical side-chain polymer DR1-MMA. The combined curing and poling processes are optimized so as to improve the thermal stability of the nonlinear optical properties. Polymer films are shown to sustain a high electro-optic coefficient of 12 pm/V at 1.32 μm during several weeks at 85 °C. An electro-optic phase modulator based on this polymer has been fabricated and demonstrated.

1. Introduction.

The limitations of current semiconductor or lithium niobate based technologies in terms of efficiency, integrability, and cost can be surpassed by calling on the remarkable properties of functionalized polymers. The major asset of this new family of materials is the unlimited flexibility of potentially available structures resulting from a predictive molecular engineering approach. Furthermore, adequately defined poling and processing technologies are shown to be compatible with hybrid polymer/semiconductor integration. We will review the linear and nonlinear properties of side-chain and cross-linked poled polymeric thin films. The wavelength dispersion of refractive index and absorption are obtained by spectroscopic ellipsometry. The second order susceptibility tensor $\chi^{(2)}(-\omega_3, \omega_1, \omega_2)$ is jointly estimated by transverse second harmonic generation ($\omega_1 = \omega_2 = \omega, \omega_3 = 2\omega$) and modulated reflection measurements ($\omega_1 = \omega, \omega_2 = \Omega, \omega_3 = \omega + \Omega$ where Ω is a modulating low frequency). Comparison between the two approaches is in keeping with a quantum two-level model of the molecular quadratic nonlinearities. Dynamical orientation and relaxation behavior is inferred from second harmonic generation combined with *in situ* corona poling. A waveguided phase modulator with 2-D confinement based on a cross-linked polymer strip waveguide over a doped silicon substrate has been demonstrated with a half wavelength voltage V_π of 30 V at 1.06 μm for an electrode length of 1.2 cm, corresponding to an r_{33} coefficient of 4 pm/V.

2. Structure of the cross-linkable polymer.

Nonlinear side-chain polymers have been widely studied over recent years towards applications in electro-optic modulation in integrated optics format. The most current side-chain polymer is Disperse-Red 1 MMA (also named DR1-MMA, shown in Fig. 1) [1]. x represents the molar concentration of chromophore in the polymer matrix. This polymer presents a high quadratic susceptibility ($d_{33} = 56$ pm/V at $1.32 \mu\text{m}$), but suffers from a low thermal stability leading to a strong decrease of the susceptibility at 70°C . This temperature is too low for telecommunication applications which require stability up to 85°C at least. In order to improve the thermal stability of DR1-MMA, a cross-linkable polymer known as « Red-acid Magly » has been synthesized and studied [2]. Its structure is shown in figure 2.

Thermal cross-linking is achieved between a carboxylic acid function (COOH) located on the nonlinear chromophore and an epoxy side group. There can be no chemical reaction between chromophores.

3. Electrical poling of polymer films.

The polymer powder is dissolved in trichloro 1,1,2 ethane at 10 % concentration in weight. One micron thick films are prepared by spin-coating (1 000 to 2 000 rpm). At this stage, the orientation distribution of the nonlinear polarizable units inside the polymer film is centrosymmetric. In order for these films to display electro-optic properties, this centrosymmetry must be broken (e.g. by electrical poling). In the case of side-chain polymers, the electrical poling procedure is achieved in two steps.

Firstly, the side-chain polymer film is heated to its glass transition temperature T_g , whereby enhancing the orientational mobility of the chromophores, which are oriented through electrostatic interaction of their dipole moment with an electric field induced either by corona discharge or by planar electrodes. In the second step, the samples are cooled down to room temperature, fixing the molecular orientation, and finally the electric field is turned-off.

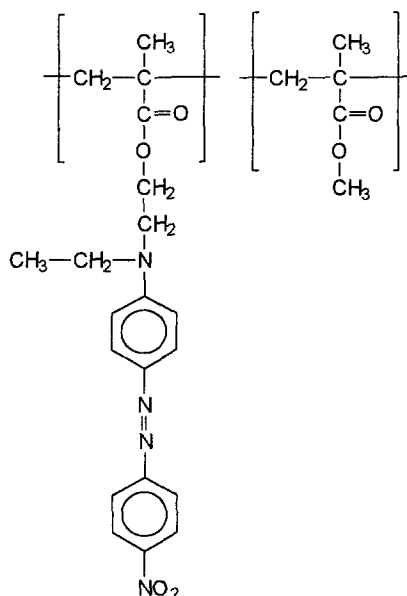


Fig. 1. — Side-chain polymer : Disperse-red 1 MMA.

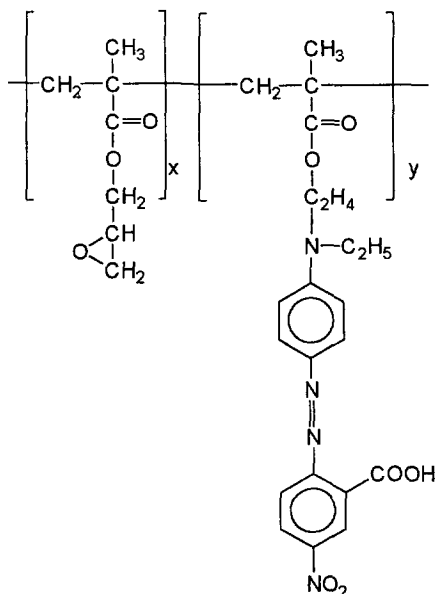


Fig. 2. — Cross-linked polymer : Red-acid Magly.

In the case of cross-linked polymers, the first step is modified since the polymer must simultaneously undergo a poling and a cross-linking process. Cross-linking will considerably improve the film stability due to the anchoring of chromophores to the polymer matrix. However this procedure also competes with the poling process since it will partly disorient the molecular dipoles as a result of chemical attachment, thus decreasing the nonlinearity of the film.

Since this competition depends on the temperature, we have further decomposed the poling and the cross-linking procedures into two steps. The first step takes place at low temperature, it favors the poling of the chromophores while the thermal cross-linking procedure remains very slow. The second step takes place at high temperature enabling complete cross-linking of the polymer while maintaining the same poling field. The optimal poling conditions are as follows :

- first the polymer is heated at 70 °C during 1 h, and the corona voltage is 5 kV. This step corresponds essentially to a poling procedure ;
- secondly the temperature is increased to 130 °C during 3 h with the same 5 kV corona discharge maintained. The polymer is thus cross-linked with the molecular dipoles oriented perpendicular to the substrate.

After these two steps, the films are cooled down to room temperature, fixing the molecular orientation, and finally the electric field is turned-off.

After cross-linking, the polymers do not dissolve in any solvent. The transparence of the film is increased, and the color turns from purple to red. The absorption spectra is shown in figure 3.

We can observe a decrease in the absorption peak and a blue shift of λ_{\max} from 520 nm to 488 nm which explains the increased transparence and the color change. In figure 4, the transmission of the polymer film at the 543 nm green line emission of a He-Ne laser is measured as a function of temperature.

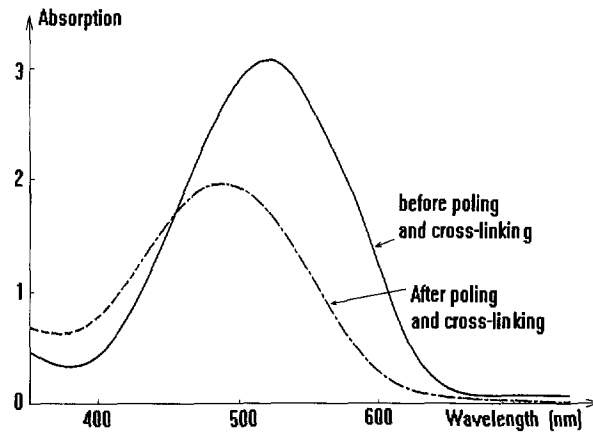


Fig. 3. — Absorption spectra of Red-acid Magly before and after poling and cross-linking measured by a spectrophotometer.

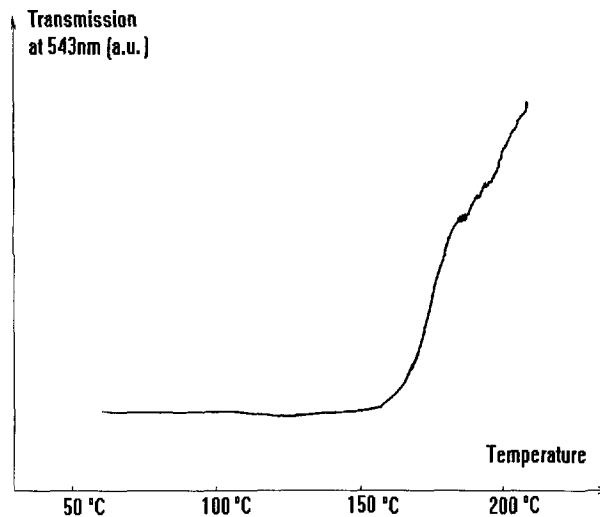


Fig. 4. — Transmission of the polymer film at 543 nm as a function of temperature (5-10 °C/mn).

The efficiency of the thermal cross-linking procedure is a function of temperature. The higher the temperature, the faster the cross-linking proceeds. We observe in figure 4 that the transparence suddenly increases at 150 °C. Table I shows the necessary duration for a complete cross-linking at different temperatures for Magly with a 30 % chromophore molar concentration.

Table I. — *Cross-link duration for Magly 30 % at different temperatures.*

Temperature	Cross-link duration
130°C	170mn
180°C	30mn
230°C	2mn

4. Ellipsometric measurements.

Spectroscopic ellipsometry is an efficient method to determine refractive index, absorption, and thickness of thin films. In table II we have listed the refractive indices at four wavelengths used in our experiments :

Table II. — *Refractive index at several wavelengths for Magly at 8 %, 17 % and 30 % molar concentrations.*

	670 nm	860 nm	1.06 μm	1.32 μm
Magly 8% (COPO1)	1.59	1.55	1.545	1.54
Magly 17% (COPO8)	1.66	1.60	1.58	1.57
Magly 30% COPO9b	1.7	1.62	1.62	1.62

We observe an increase in the refractive index with the concentration. The spectroscopic dispersion curves of the refractive index n and the absorption coefficient k of Magly 30 % are shown in figure 5. Real and imaginary parts of the refractive index follow the Kramers-Kronig relation. The ellipsometric absorption curve is in good agreement with the direct absorption measurement shown in figure 3.

5. Second harmonic generation characterization of the thermal stability.

The stability of the polymer films was investigated by measuring the quadratic susceptibility involved in the second harmonic generation of a 1.32 μm YAG laser.

Second harmonic generation is a reliable method to characterize the nonlinear properties of polymer films. The signal detection is much more sensitive and is purely nonlinear as opposed to the modulated reflection method, described in the next paragraph, which may contain electrostrictive contributions.

An important short term decay of the quadratic susceptibility d_{33} of a DR1-MMA film (29 % molar concentration) as measured by the SHG method at 1.32 μm is evidenced in table III, where we compare the d_{33} values just after poling and 24 h after poling at room temperature. The chromophore relaxation brings down the non linear efficiency by almost 50 % over the 24 h following poling and is stabilized then. On the contrary, no significant decay could be observed for Red-acid Magly in the same conditions, showing that short term relaxation in these cross-linked polymers is much weaker than in the analog side-chain polymers.

In order to assess the thermal stability of polymer films, the SHG response from a polymer film heated *in situ* is measured at a constant heating rate. The curves of SHG signal $I_{2\omega}$ as a function of temperature for DR1-MMA 29 %, Magly 17 %, and Magly 30 % are shown in figure 6.

Thermal stability is much higher in the case of Magly 30 % : for the same amplitude of $I_{2\omega}$, a 30 °C improvement can be noted.

The aging of the different polymers was also investigated in function of time at different temperatures. Figure 7 shows the decay of d_{33} (1.32 μm) as a function of time at the decay temperature of 55 °C for DR1-MMA 29 % and at 85 °C for Magly 30 %. Magly 30 % has a good stability at 85 °C whereas DR1-MMA 29 % displays about the same stability only up to 55 °C. A 30 °C improvement in thermal stability is observed here again when comparing the stability of the side-chain polymer to that of the cross-linked polymer.

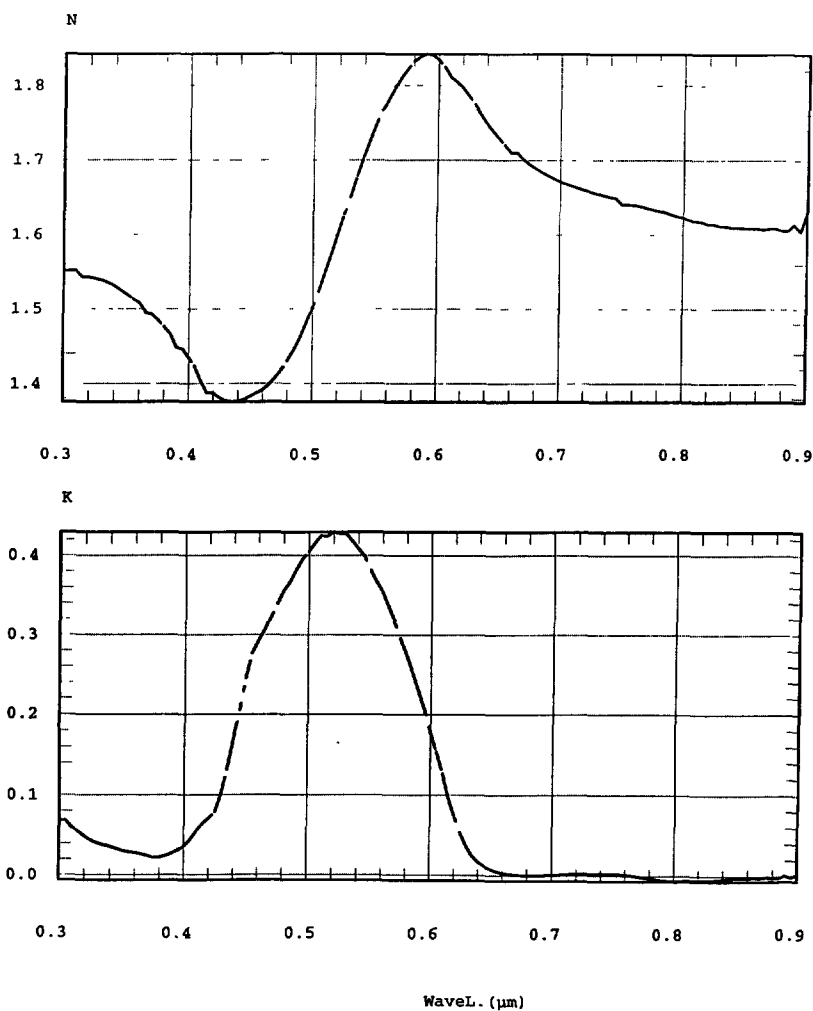


Fig. 5. — Spectral dispersion of the refractive index and absorption coefficient of Magly 30 % from 0.3 μm to 0.9 μm as measured by ellipsometry.

Table III. — d_{33} values just after poling and 24 hours after poling at room temperature.

	d_{33} poling at 120°C for 15mn	d_{33} 24h after poling at room temperature
DR1-MMA 29%	56pm/V	29pm/V

We also measured the susceptibilities of different copolymers of Red-acid Magly type prepared with different chromophore concentrations : 8 %, 17 % and 30 % and compared them to DR1-MMA 29 %.

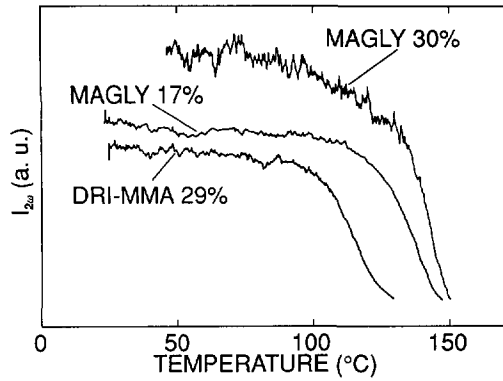


Fig. 6. — Thermal behavior of DR1-MMA 29 %, Magly 17 %, and Magly 30 %.

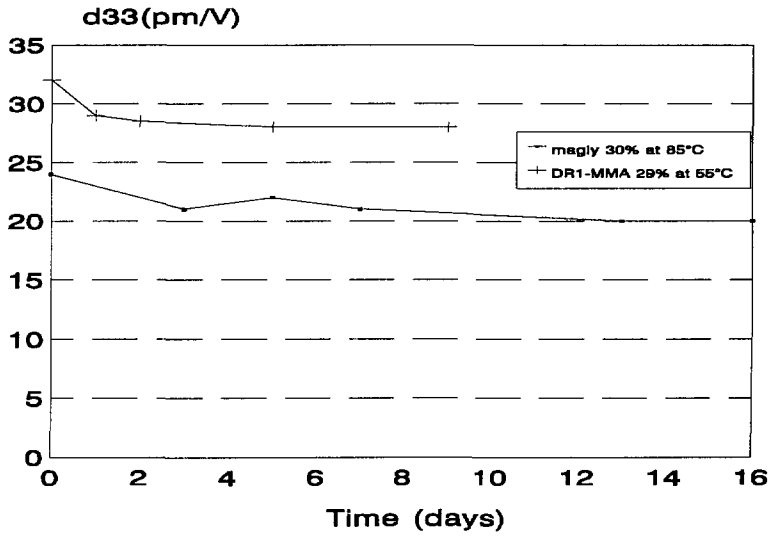


Fig. 7. — Temporal stability of the quadratic susceptibility d_{33} as a function of time at $1.32 \mu\text{m}$ for DR1-MMA 29 % at the decay temperature of 55°C and for Magly 30 % at 85°C .

Table IV. — d_{33} and d_{13} values of DR1-MMA 29 % and Red-acid Magly at different molar concentrations at $1.32 \mu\text{m}$.

polymer	d_{33}	d_{13}
DR1-MMA 29%(relaxed)	29pm/V	-
Magly 8%	10.2pm/V	-
Magly 17%	24pm/V	-
Magly 30%	29pm/V	9.5pm/V

This shows that d_{33} increases linearly with the chromophore concentration from 8 % to 17 %. The interaction between chromophore dipoles rises as the chromophore concentration increases, deviates therefore the theoretical linear relationship [3] as observed for d_{33} of Magly

30 %. Comparing d_{13} and d_{33} of Magly 30 % shows that the d_{33}/d_{13} ($= 3$) ratio agrees well with the results of a one-dimensional molecular model [4] for this cross-linked polymer with the process we have used.

6. Electro-optic coefficient measurement.

For the determination of the electro-optic coefficient r_{33} , we have used a modulated reflection method [6], in which the electro-optic coefficients $r_{33} - r_{13}$ are deduced from the modulation of the intensity of low power cw laser beams reflected by the samples under test. It remains a fast assessment technique which provides the electro-optic coefficient of polymer films to be compared to the susceptibilities obtained from SHG measurements.

The measurements, carried out at two wavelengths after eventual short term relaxation of the molecular orientation, for DR1-MMA 29 % and Magly 30 %, give about the same results for both types of polymers :

Table V. — *Electro-optic coefficients r_{33} of DR1-MMA 29 % and Magly 30 %.*

	r_{33} at 1064nm	r_{33} at 1320nm
DR1-MMA 29%	13.5 pm/V	12.4 pm/V
Magly 30%	14.8 pm/V	12.6 pm/V

The quantum two-level model of the molecular quadratic nonlinearities [6] leads to the following relation between the second harmonic coefficient $\chi_{::}^{(2)}(-2\omega; \omega, \omega)$ and the electro-optic coefficient $r_{33}(-\omega; \omega, 0)$.

$$r_{33}(-\omega; \omega, 0) = -\frac{2}{n_\omega^4} \frac{f^0}{f^{2\omega}} \frac{(3\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)}{3\omega_0^2(\omega_0^2 - \omega^2)} \chi_{::}^{(2)}(-2\omega; \omega, \omega)$$

where ω is the fundamental laser frequency, ω_0 is the absorption peak frequency of the polymer, n_ω is the refractive index at frequency ω and $f^{2\omega}$ (resp. f^0) are Lorentz-Lorentz (resp. Onsager) local field factors given by :

$$f^\omega = \frac{n_\omega^2 + 2}{3} \quad f^0 = \frac{\varepsilon(0)(n^2 + 2)}{2\varepsilon(0) + n^2}$$

and $\varepsilon(0) \sim 4.5$, $\chi_{::}^{(2)}(-2\omega; \omega, \omega) = 2d_{33}$.

Experimental d_{33} (29 pm/V) and r_{33} (12.6 pm/V) values are in good agreement with this model for the cross-linked polymer.

7. Electro-optic phase modulator.

The electro-optic properties have been further demonstrated in phase modulator device configurations achieved in linear strip waveguides. The fabrication process of this type of strip waveguide is summarized in figure 8. The main successive steps are as follows : spin-coating, photolithography, and reactive ion etching techniques [7]. The bottom buffer layer is made of SOG (Spin On Glass), a commercially available Allied Chemical product. The polymatrif upper buffer layer is an Atochem research product. The guiding layer is Magly 30 %. The electrical poling process occurs at step 2 under the optimal conditions mentioned previously. In step 3, a classical photolithography process, usually used for microelectronics, was applied over the nitride (Si_3N_4) layer. The photosensitive resin is spin-coated and insulated through a

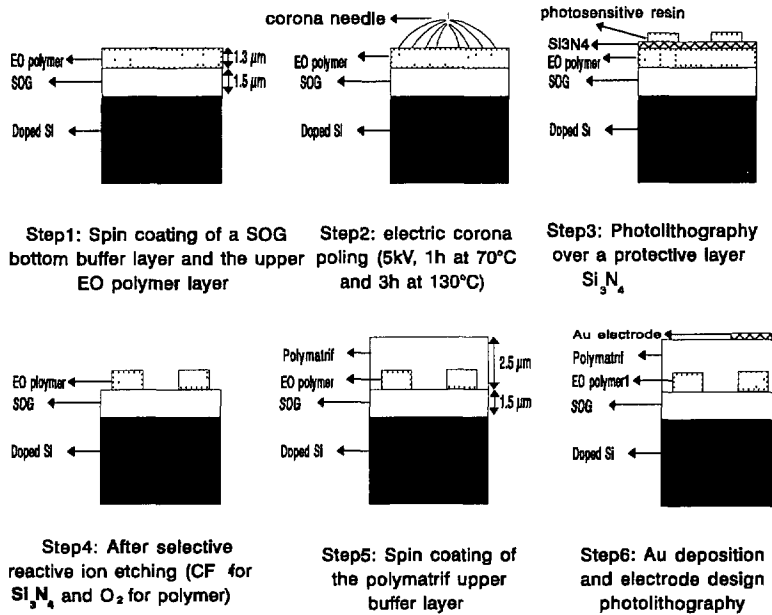


Fig. 8. — Fabrication process of strip polymer waveguide.

mask with UV light. The insulated resin was dissolved with a developer. Thus, we obtained the structure shown in step 3 of figure 8. To obtain step 4, the selective reactive ion etching technique is used. Two plasmas, namely O_2 and CF_4 , were chosen to etch selectively the organic layers (the photosensitive resin and the electro-optic polymer) and the Si_3N_4 layer. The sample is plasma etched three times : first based on the structure of step 3, CF_4 plasma is used to etch the exposed Si_3N_4 section with no photosensitive resin on top. The O_2 plasma is then used to etch the organic material layers (i.e. the photosensitive resin and the electro-optic polymer). CF_4 is then used again to etch the Si_3N_4 just over the electro-optic guide core.

A polymatrif layer is spin-coated and cured back at 90 °C. In step 4, a passive polymer waveguide is obtained. A propagation loss of 2 dB/cm or less in these optical waveguides is measured by the cut-back method. A 1 000 Å-thick gold electrode is deposited by evaporation, with a final photolithographic step using a thicker photosensitive resin and an electrode pattern mask. After photolithography, a potassium iodide solution removes the gold not covered with resin. Another UV insolation and application of developer cleans the residual resin over the gold electrode. An electro-optic polymer modulator is obtained at step 6.

These steps applied at 100 °C for about 3 h should not destroy the electro-optic properties of the film. This method is only valid for electro-optic polymers thermally stable at 100 °C. For an electro-optic polymer unstable at 100 °C, like DR1 side-chained PMMA, electrical poling is only applied at the end of the fabrication process, after step 6.

The best figures obtained so far at 1.06 μm are $V_\pi = 30$ V for the phase modulator inserted between crossed polarizers. V_π represents the voltage necessary to produce an electro-optic effect-induced phase difference of π between the TE and TM modes. Electro-optic modulation was also observed at 1.32 μm . The experimental set-up and the electro-optic modulation signal is shown in figure 9.

The r_{33} value in the phase modulator inferred from the relation $r_{33} = 3 h \lambda / 2 V_\pi L n^3$ is on the order of 4 pm/V. Where h is Planck constant, λ is the laser wavelength and n is the waveguide

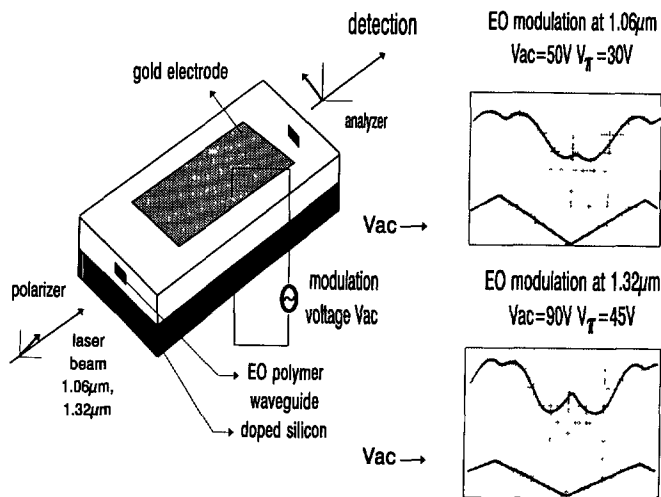


Fig. 9. — V_{π} measurement in a linear waveguide phase modulator at wavelengths : 1.06 μm , 1.32 μm .

refractive index. This value is weaker than in table V for two reasons : thermal disorientation during the waveguide fabrication process (3 h at 100 °C) and weaker poling efficiency for multilayers (step 2 in Fig. 8) than for single layers in thin film measurement.

8. Conclusion.

In conclusion, we have evidenced the improved stability of a thermally stable cross-linked nonlinear polymer and demonstrated a waveguide phase modulator based on this polymer. The polymer used maintains its electro-optic coefficients over at least several weeks at 85 °C. This efficiency-stability trade-off is believed to correspond to the current optimum for this class of materials and devices. A decrease of V_{π} by a factor of 3 to 4 can be expected from further optimization such as a higher poling efficiency and a still better thermal stability of the cross-linked polymer.

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