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Liquid Crystals

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Invited Lecture

Properties of side chain liquid crystal and amorphous polymers

Applications to non-linear optics

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Comb-like liquid-crystalline polymers exhibit many unique properties that challenge not only basic research but also numerous technological opportunities. They combine (partly) the properties of orientation of low molecular weight liquid crystals with the rigidity of polymers. For example, they can be oriented in the mesomorphic state and the structure frozen in a glassy state. These polymers with functionalized pendent groups lead to potential applications in the field of nonlinear optics, or in the domain of electro-optical displays. Other polymers like polysilanes show interesting properties such as photo-conductivity. This paper describes the properties and applications of some new side chain liquid-crystalline polyacrylates and their amorphous copolymers. It also describes the photoconductive properties of polysilanes and their applications in spatial light modulators with liquid crystals. In the first part of this paper, we describe the properties of liquid crystal copolymers and amorphous polyacrylate copolymers with cyanobiphenyls and/or pendent groups with a large hyperpolarizability. Their different properties are compared with some recent results from the literature. These amorphous copolymers allow one to obtain, after poling in an electric field, high optical non-linear coefficients. We have used these copolymers for the manufacture of an electro-optic modulator working at $1.3 \,\mu\text{m}$ in the frequency range of 1 GHz. Applications to second harmonic generation at $1.06 \,\mu\text{m}$ are also discussed. In the second part of this paper we describe the photo-conductive properties of polysilanes and the realization and performance of an organic spatial light modulator for optical correlation.

1. Introduction

Polymers and specially side chain polymers, liquid-crystalline or amorphous, can be used in optics and optoelectronics [1]. They are almost ideal systems because they can be oriented by an electric field and the orientation frozen into a glassy state [2–5]. In this case they can show interesting optical non-linear properties. Such systems can be used to influence and control the temporal, spatial, and frequency properties of propagating light beams and are, therefore, important for optical processing purposes. Their optical properties have been extensively studied and show great potential for use in electro-optic or frequency doubling devices [6]. Polymers, also, can be deposited by using processes completely compatible with silicon technologies. But in order to achieve such devices, the quality of the polymers has to be improved. Different routes

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have been tried to reach this goal, in particular with side chain liquid crystal and also amorphous polymers [7]. In the first part of this paper we will describe the properties of these polymers with quadratic non-linear effects and the performance of polymeric devices: frequency doubling (second harmonic generation: SHG) and electro-optic modulation.

Other polymers like poly(methyl phenyl)silane show, after doping, interesting photo-refractive and photo-conductive properties [8]. In association with a nematic liquid crystal, this polymer has been used for realization of a spatial light modulator. This modulator has been integrated in an optical Fourier transform correlator for pattern recognition. The description and performance of this modulator will be given in the second part of this paper.

2. Side chain polymers for quadratic non-linear effects

2.1. NLO properties of organic materials

The non-linear optic is primarily concerned with the response of a dielectric material to a strong electromagnetic field. The polarization μ thus induced in a molecule can be written as

$$\mu = \mu_0 + \varepsilon_0 (\alpha E + \beta E E + \gamma E E E \dots), \tag{1}$$

where E is the optical electric field, β and γ are the second and third order non-linear optical hyperpolarizabilities.

The induced polarization P in a macroscopic medium can be similarly expressed by

$$P = P_0 + \varepsilon_0 (\chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE \dots),$$
(2)

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibilities.

In order to obtain a useful material possessing a large second order non-linear susceptibility tensor $\chi^{(2)}$, one requires the use of molecules with a large microscopic second order non-linear hyperpolarizability tensor β organised in such a way that the resulting system has no centre of symmetry and an optimized constructive additivity of the molecular hyperpolarizabilities. In addition, the ordered structure thus obtained must not exhibit a loss of non-linear optical properties with time. The non-linear optical materials which have been synthesized so far, derive from the donor- π -system-acceptor molecular concept (see figure 1).

STRUCTURE OF CONJUGATED MOLECULES FOR β VALUES



Figure 1. Basic molecular structure for quadratic non-linear effects.

Successful approaches to increase the hyperpolarizabilities of non-linear optical moieties have been achieved by using strong electron donor and electron acceptor groups and by increasing the conjugation length [9]. But, depending on the input laser wavelength used and the type of application considered (electro-optic modulation or frequency doubling), a compromise has to be found between transparency and non-linearity.

Macroscopic organization of non-linear optical moieties, suitable for quadratic applications are currently obtained from:

single crystals, Langmuir-Blodgett multilayers, polymer films.

Growth of single organic crystals is difficult in thin films and Langmuir-Blodgett films induce important losses by scattering. Polymers and especially side chain polymers seem to be the best candidates to meet the requirements of integrated nonlinear optics, since they are compatible with semiconductor technology. Owing to the spin-coating techniques, low cost thin films can be obtained for waveguide applications. Moreover, they have the advantages of organic materials, namely:

high non-linear coefficients, fast response time, high optical damage threshold, high potential for molecular engineering.

Three classes of quadratic non-linear optical polymers have been investigated so far:

side chain liquid crystal polymers, ferroelectric polymers, amorphous polymers.

Side chain liquid crystal polymers and moreover amorphous polymers seem the most promising class of polymeric materials for non-linear optic applications.

Whatever the type of polymer used, a film about 1 μ m thick has to be deposited on to a substrate via spin coating or dipping techniques. After deposition, the film is centrosymmetric. In order to get a non-centrosymmetric system, a DC external electric field must be applied at a temperature which allows free orientations of the non-linear optical group (generally above the T_g of the material). After cooling at room temperature in the electric field, poling provides the alignment predicted by the Boltzmann's distribution law and imparts a $C_{\infty v}$ symmetry to the film (see figure 2). Pioneering work was done by orientation of a dye like p' dimethylamino-pnitrostilbene (DANS) in an amorphous polymer like polymethyl methacrylate (PMMA) by Havinga in 1979 [10].

2.2. Side chain liquid crystals polymers

In 1982, Meredith demonstrated that better results could be obtained using a nematic side chain polymer host [11] (see figure 3). In fact keeping the orientational order with such a low T_{e} was not possible ($T_{e} < 50^{\circ}$ C).

By doping, there is also the difficulty of increasing the content of dye due to its poor solubility. For these reasons of stability and the concentration of dopant, many authors have synthesized amorphous copolymers with one of the comonomers bearing the active dye as a pendent moiety [9]. Figure 4(a) shows the relative evolutions with time



Figure 2. Electric field induced orientation of non-linear optical moieties in a polymer (poling process) where T_p is the poling temperature.

NEMATIC POLYMER (HOST)



Figure 3. Example of a guest-host system [II] for quadratic effect using a Dye (DANS) 2 per cent by weight in a nematic polymer. g is the glass transition, N nematic state, E_p , the poling electric field, is $1.3 \text{ V} \,\mu\text{m}^{-1}$ and $\chi^{(2)}$ the second order susceptibility is 6×10^{-9} esu.

of the d_{33} values (second harmonic coefficients determined after poling) for the copolymer and the corresponding guest-host doped polymer PMMA. The d_{33} (or more precisely the orientation) is much more stable for the copolymer (see figure 4(b)) [12]. A certain amount of research has been done since then in this area, e.g. the synthesis and study of side chain liquid crystal polymers (SCLCP) with an active pendent group (donor-acceptor) [1, 13-15]. We describe now some of these results.



Figure 4. (a) Decay of the second-harmonic coefficient of DCV-MMA Polymer (●) and DCV in PMMA (□) (corona-poled films). (b) The chemical structure of the DCV-MMA copolymer [12].



Figure 5. Different nematic polymers for $\chi^{(2)}$ measurements synthesized in [17].

Griffin *et al.* have reported the copolymers shown in figure 5 [16, 17], and we have published some results on the copolymers in figure 6 [18, 19], but we did not get good results, since, in general, these polymers scatter light after polarization and optical losses are important due to the difficulty of orientation.

Recently, other authors have succeeded in synthesizing high T_g side chain liquid crystal polymers and have obtained better results. For example, McCulloch (see figure 7) [20] and other authors have measured d_{33} in the order of 8 p mV⁻¹ at 1.31 μ m with corona poling.



Figure 6. Different nematic copolymers synthesized in [13] and [1].



= 29.1 10⁻³⁰ cm⁵ esu (à λ = 1.91 μ m)

g 85 S_A 165 I

Гр = 50°С	CORONA		
		d ₃₃ = 8.4 pmV ⁻¹	$\lambda = 1,319 \mu m$
n _{1.047} ∎ 1,65	2	20 dB cm ⁻¹	
n _{1.047} = 1,65		7 dB cm ⁻¹	

Figure 7. Smectic A copolymer synthesized [20] for $\chi^{(2)}$ and d_{33} measurements. Poling is made by corona at a temperature $T_p = 50^{\circ}$ C, $d_{33} = 8.4 \text{ pmV}^{-1}$ at 1.319 μ m.

Amano (see figure 8) [21] has found that $\chi^{(2)}$ of liquid crystal polymers should be higher ($\chi^{(2)}_{LCP} = 1.5\chi^{(2)}$ amorphous) than for the corresponding amorphous polymer. Koide found similar results ($\chi_{LCP}^{(2)} = 1.2\chi^{(2)}$ amorphous) (see figures 9 and 10) [22], and other authors have examined chiral smectic C* copolymers [23-25].

It seems however that these different studies, including our own research, demonstrate that higher optical losses and greater difficulties of orientation occur with side chain liquid crystal polymers than with amorphous polymers.

2.3. Amorphous polymers with active pendent groups for second harmonic generation

A natural step towards highly efficient and stable non-linear optical polymers was the synthesis of covalently functionalized amorphous polymers. By linking the dye directly to the polymer backbone, it is possible to achieve high chromophore densities



Figure 8. The value of $\chi^{(2)}$ of the poled nematic polymer [21] is 1.5 times higher, $\chi^{(2)}=8 \times 10^{-9}$ esu, than the corresponding poled amorphous polymer when a poling field, E_p , of $15 \,\mathrm{kV \, mm^{-1}}$ is used.



Figure 9. Variation of $\chi^{(2)}$ in a copolymer [22] versus the value x of nitro-comonomer. For x = 0.8 the value of $\chi^{(2)}_{1,CP}$ is equal to the value of $\chi^{(2)}_{2}$ amorphous.



Figure 10. Mesomorphic polymer [20]. The value of $\chi^{(2)}_{LCP}$ was found to be 1.2 times higher than $\chi^{(2)}$ for the amorphous copolymer.

(without phase separation) and to increase the temporal stability of the poled material. Covalently functionalized amorphous polymers can be obtained either by copolymerization of a monomer bearing the chromophore unit via a flexible spacer group with a comonomer contributing to the amorphous character of the final copolymer [26] or by modifying a reactive polymer such as poly-(p-hydroxystyrene) [27], poly-(methyl methacrylate-co-(N-ethylanilino) ethyl methacrylate) [11, 28], poly-(hydrogen methyl siloxane) or poly-(allylamine hydrochloride [29]. Chromophore functionalization levels from 0 to 100 per cent can thus be achieved at will.



Figure 11. Phase transitional behaviour of liquid crystal polymers with cyanobiphenyl pendent chains [12].

The temporal stability of the orientational ordering after poling has been investigated and the d_{33} decay can be written as

$$d_{33} = \underbrace{A \exp(-t/\tau_1)}_{\text{Fast component}} + \underbrace{B \exp(-t/\tau_2)}_{\text{Slow component}}$$
(3)

 τ_1 and τ_2 are respectively the short-term and the long-term second harmonic generation decay lifetimes [27].

Following our studies on liquid crystal polymers with cyanobiphenyl as the pendent group [13] (see figure 11), we have synthetised and studied amorphous copolymers with pendent groups of related type for second harmonic generation. The main property to be fulfilled for second harmonic generation is polymer transparency in the visible region. This leads to the following limitations on the maximum absorption of the non-linear optical unit for:

green laser source application (at 1.06 μ m input laser) $\lambda_{max} < 350$ nm, blue laser source application $\lambda_{max} < 300$ nm.

For the green source, one of the pendent groups is based upon 4-dimethylamino-4'cyanobiphenyl

 $\begin{array}{c} \text{CH}_{8} \\ \text{N} \\ \text{CH}_{8} \end{array} \xrightarrow{} \begin{array}{c} \mu = 6 \text{ D} \\ \beta_{0} = 32 \, 10^{-30} \text{ esu} \end{array}$

and leads to the polymer in figure 12, with $d_{33} = 12 \text{ pmV}^{-1}$ (twice the coefficient of LiNbO₃...), N = 1.05 × 10²¹ molecules/cm³, and λ_{max} : 348 nm. With this polymer, in a waveguide structure, Lemoine [30] has obtained a frequency doubler (green source) with a 5 mm length waveguide, with a ratio of $\rho^{2w}/(\rho^w, L)^2 = 2 \times 10^{-3} \text{ per cent/W/cm}^2$.

However, for the blue source, λ_{max} has to be decreased and the chosen pendent groups are



Figure 13 summarizes the results.



Figure 12. Structure of an amorphous copolymer for frequency doubling [30].



Figure 13. Amorphous copolymers for green or blue laser source.

2.4. Amorphous polymers with pendent group for electro-optical modulation The variation of refractive index in a polymer as a function of the electric field can be written

$$\Delta(1/n^2)_{ij} = r_{ijk}E_k + s_{ijkl}E_kE_l, \tag{4}$$

where r_{ijk} and s_{ijkl} are respectively the linear electro-optic (Pockels) coefficient and the quadratic (Kerr) coefficient. E_k is the kth component of the electric field applied to the structure. The elements of the tensor (s) being smaller than the elements of the tensor (r), the quadratic effect can be neglected.

The electro-optic coefficient can be related to the second order susceptibility by

$$\chi_{ijk}^{(2)}(-\omega,\omega,0) = -1/2[n_{ii}^{2}(\omega)n_{jj}^{2}(0)] \cdot r_{ijk}(-\omega,\omega,0),$$
(5)

This expression shows that the electro-optic coefficients are proportional to the second order susceptibility. Values of r_{33} corresponding to d_{33} can be calculated and measured. Examples of values for one of our polymers are in figure 14.



Figure 14. Relationship between r_{33} and d_{33} in copolymers.



Figure 15. Structure of a planar electro-optic modulator used for measuring electroptic coefficient and optical refractive indices.



Figure 16. Active polymer for electro-optic modulator at 0.632 μ m where x = 0.35, $T_g = 111^{\circ}$ C, $d_{33} = 13 \text{ pmV}^{-1}$, $r_{33} = 7 \text{ pmV}^{-1}$, $V_{\pi} = 13 \text{ V}$ and $\lambda_{\text{max}} = 370 \text{ nm}$.

An electro-optic modulator defined as a waveguide structure can be characterized by four principal criteria: modulating voltage, bandwidth, power requirement and propagation losses. The modulating voltage required for total extinction V_{π} is [30]

$$V_{\pi} = \frac{\lambda}{n^3(r_{33} - r_{13})} \times \frac{e}{l},\tag{6}$$

with e = thickness, l = length, n = refractive index, $\lambda =$ wavelength, r_{33} , r_{13} electro-optic coefficients of the polymer.

Achievement of an electro-optic modulator operating over the range $(0.8-1.6 \mu m)$ and activated by an electric field requires the use of polymers with high electro-optic coefficients and low absorption losses. Polymers are however sufficiently flexible to permit the realization of a trade off between high electro-optic efficiency and low absorption losses. Authors [31, 32] have already reported large values of electro-optic coefficients (50 pm/V), but the values measured for optical structures are generally lower (5–20 pm/V). Indeed for use as integrated waveguides low absorption losses are required. Therefore such high values of r_{33} obtained near the absorption band cannot be used because of high absorption losses associated with the resonant effect. Figure 15 shows a typical structure composed of three layers spin-coated on a conductive silicon substrate. This modulator operates by using the differential birefringence electrically induced between TE and TM.



Figure 17. Active polymer [26] for electro-optic modulator at 1.32 μ m where $T_g = 126^{\circ}$ C, $r_{33} = 10 \text{ pmV}^{-1}$ and $V_{\pi} = 20 \text{ V cm}$.

We have made different side chain amorphous polymers for electro-optic modulators working in two wavelengths, $\lambda_1 = 0.632 \,\mu\text{m}$ and $\lambda_2 = 1.319 \,\mu\text{m}$. The polymer shown in figure 16 is specially designed for use at $0.632 \,\mu\text{m}$ in an electro-optic modulator and has the following properties $r_{33} = 7 \,\text{pmV}^{-1}$ and $V_{\pi} = 13 \,\text{V}$ cm. Similar results have been obtained with a polymer (see figure 17) at $1.32 \,\mu\text{m}$. The stability of the electro-optic coefficient can be further improved by using crosslinking of the pendent units. This work is in progress at Thomson's laboratories elsewhere.

3. Spatial light modulator-photo-conductive polysilane liquid crystal

Polysilanes are attractive photo-conductive polymers; the mobility of charge carriers is high, but a dopant is necessary to enhance the sensitivity in the visible wavelength range. We have synthesized and doped these polymers and we describe here their use in association in a spatial light wave modulator.

Polysilanes are made by polycondensation reactions, e.g., of dichloromethylphenylsilane in the presence of sodium using ultrasound (see figure 18). The polymer, $T_g \approx 120^{\circ}$ C and having an average molecular weight of Mn $\approx 2 \times 10^5$, is an attractive photo-conductor due to the high mobility of the charge carrier (mobility 10^{-3} cm² V⁻¹ S⁻¹). This feature has been related to the ability of holes to be displaced along the silicon backbone via the overlap of the Si–Si orbitals. In order to obtain photo-conductivity in the visible region, it is necessary to sensitize the polymer. We have done this by using non-metalated phthalocyanines [8].

Organic spatial light modulators are potentially of great interest for parallel processing applications such as optical pattern recognition, demanding high volume operation. Spatial light modulators based on a photo-conductor-liquid crystal layered structure have been widely investigated [33]. One of the main goals was to achieve high resolution, which requires the photo-conductor to have a low thickness and a high dark-level resistivity. Polymeric photo-conductors, and particularly doped polysilanes exhibit promising features compared to a photo-refractive correlator [34].

The layered structure of the photo-conductor-liquid crystal cell is shown in figure 19. In the regions illuminated by the writing beam (in the absorption band of the photo-conductor), the voltage is transferred to the liquid crystal, which induces a birefringence. The birefringence changes are read by a reading beam. The polysilane is doped with 30 per cent of phthalocyanine. The nematic liquid crystal is Merck 3651 chosen for its low dielectric anisotropy and its high resistivity ($\rho > 10^{12} \Omega$ cm).

Figure 20 presents the change in diffraction of the spatial light modulator positioned in an interference field obtained by mixing two planar waves. The x-axis corresponds to the spatial frequency in mm⁻¹, that is to say the inverse of the network pitch. The y-axis is a diffraction yield, the ratio between the 1st order and 0 order intensity expressed as a percentage. A spatial resolution less than $10 \,\mu\text{m}$ is then measured for a diffraction yield of 5 per cent.

The structure of the optical correlator using the new spatial modulator is represented in figure 21. The two patterns to correlate (reference R and unknown object S), issued from two video cameras, are written (R + S) on a liquid crystal screen display, electrically addressed (EA-SLM commercially available). They are read by a beam from a mini-YAG laser ($\lambda = 532$ nm). A Fourier lens L1 set behind this first modulator gives in its focal plane the Fourier transform of the image to be analysed and of the reference image. The two beams interface in this plane in producing a figure of fringes whose frequency depends on the splitting between the two images and for which the modulation ratio is proportional to the product of their Fourier transforms:



Figure 18. Principle of synthesis and molecular weight repartition of the poly(methylphenyl) silane [8] where $T_g = 120^{\circ}$ C and the yield is 15 per cent.



Figure 19. Structure of the photoconductor-liquid crystal cell.



Figure 20. Evolution of the diffraction yield (Y) as a function of the spatial frequency (X) (in mm⁻¹).



Figure 21. Structure of optical correlator using new spatial modulator.

 $\mathscr{F}(\mathbf{R}) \cdot \mathscr{F}(\mathbf{S})$. The spatial light modulator polysilane-XL (PSi-SLM) is placed in this focal plane. Through the intermediate of the photo-conducting polymer the interference fringes are transcribed on the liquid crystal. A refractive index modulation which varies from the ordinary index ($n_0 = 1.49$) to the extraordinary index ($n_e = 1.59$) is thus induced. The interference fringes are then revealed in the form of a hologram, recording information which is proportional to the product of the Fourier transforms of the image to be analysed and the reference image. It is then sufficient to read this



Figure 22. Determination of an object by consideration of the position of its correlation peak in the output phase.

hologram with a planar wave ($\lambda = 633$ nm) in order to obtain this product. One realizes then the reverse Fourier transform with the second lens L2 and obtains in its focal plane the correlation function $R \times S$ between the image to be analysed and the reference image.

Figure 22 illustrates some experimental results. The reference images consist of four different objects. The object to be analysed is one of these four and one can see a correlation peak in the output plane. Its position allows us to determine the unknown object. Future studies will allow us to determine the change of intensity of the correlation peak when the object undergoes a change of scale or angular position.

Preliminary studies have however allowed us to compare the PSi-SLM to photorefractive non-linear materials which have been used up to now [35]. The results show that one can expect good performances from this new type of modulator (see table). Many characteristics are in favour of the new PSi-SLM correlator, such as:

high photo-induced modulation,

large size due to possibility of spin coating the polymer, low applied voltage.

However, the polymer has still to be improved and, in particular, the sensitivity has to be increased by choosing better dopants.

	Photorefractive correlator	Organic spatial light modulator
Photoinduced index modulation	$10^{-5} - 10^{-3}$	10 ⁻¹
Size	$1 \times 1 \text{ cm}$	Few cm ²
Applied voltage	Few kV, DC	10 V, AC
Angular tolerance	Few degrees	> 30°
Cost	High (2 KECU)	Low (?)
Resolution (at 10^{-3} diffractive efficiency	$< 1 V \mu m$	$1-2 \mu m$
Sensitivity (green)	$1-10 \mathrm{mW}\mathrm{cm}^{-2}$ (40 ms)	$100 \mathrm{mW}\mathrm{cm}^{-2}$ (40 ms)

A comparison of performances between the photorefractive and PSi-SLM correlator.

4. Conclusion

The good active properties of polymers allow the realization of many applications in the field of electro-optics. From the first steps in molecular engineering of some ten years ago to devices with non-linear polymers, the gap has been quickly bridged. The side chain polymers allow the realization of low loss (1 dB/cm) electro-optic modulators with $V_{\pi} < 10$ V operating at high frequency and represent probably one of the most promising applications. In second harmonic generation in the blue green range, the results are less good and more studies have to be made.

Polymers, with their unique ease of processability have good potential for use in different electro-optic devices. The polysilane-liquid crystal spatial light modulator is another example of what can be done in this area and the great potential for development.

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