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PROPERTIES AND APPLICATIONS OF POLYMERS IN ELECTRO-OPTICS

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Abstract Polymers combine the possibility of easy processing with an infinite potential of functionalization. They have long been used as passive materials for components in electronics and electrooptics. They can be conductors or semiconductors, ferroelectrics and can exhibit interesting properties such as photoconductivity, piezo or pyroelectricity or nonlinear optical properties. As a consequence they are now used for merging active components in such fields of electrooptics as displays, sensors or modulators for optical signal treatment. This paper intends to review the properties and applications of some recent polymers in the field of electrooptics. In the first part of this paper we describe the properties of amorphous copolymers with a pending group with large hyperpolarizability. These amorphous copolymers show high electrooptical coefficients and we have used these copolymers for the realisation of an electrooptic modulator. Spatial light modulator used for pattern recognition formed with the association of a polysilane and a liquid crystal cell is also described. The second part deals with ferroelectric polymers and their pyroelectric properties. We describe the realisation and performance of an IR pyroelectric sensor using copolymers of polyvinylidene fluoride-ethylene trifluoride. In the third part, we describe the results of our work on polymer dispersed liquid crystals (PDLC), their preparation by photopolymerisation and their performances for displays.

INTRODUCTION : ORGANIZED MOLECULAR MATERIALS

Organic organized molecular materials show interesting properties which can be used in electrooptics.[1,2,3]. Liquid crystals are one example of such materials with their well known use in the field of displays with the development that can be seen at present.

The organization of active moieties of molecule can be obtained by several different types of systems such as (Figure 1) :

- single crystals
- Langmuir Blodgett Layers
- or polymer films.

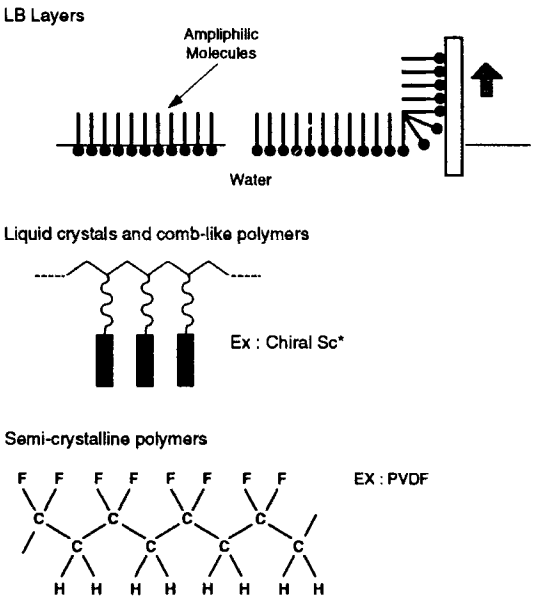


FIGURE 1 Organized molecular systems

This paper reviews some of the properties and applications of the polymers films which can be either liquid crystal, amorphous or semi-crystalline. For example, the organization in the poly(vinylidene difluoride) PVDF (polymer) leads to the interesting properties of ferroelectricity.

Another example concerns the comb-like polymers Figure 2 where the choice of the pending group and the addition of a chiral group lead to liquid crystal polymers which exhibit chiral C phase that can be of potential use in polymer displays.

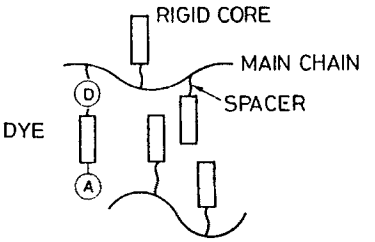


FIGURE 2 Lateral chain polymers or comb-like polymers

We have evaluated different kinds of these organized polymers and used these polymers for different applications that we would like to review here. These polymers are :

- amorphous polymers for electro-optic modulators
- photoconducting polymers and liquid crystals for spatial light modulators
- ferroelectric polymers for infrared detection
- liquid crystal and polymer dispersed liquid crystals for displays. These applications are described here as example of what can be obtained with organic "active" materials.

AMORPHOUS POLYMERS FOR POCKELS EFFECT

The variation of refractive index in a polymer as a function of the electric field can be written :

$$\Delta (1/n^2)_{ij} = r_{ij} E_k + s_{ijkl} E_k E_l$$

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

Values of the component of the (r) tensor r_{33} and r_{13} can be calculated and measured. There is a relation of proportionality between r_{ijk} and the d_{ijk} coefficient of the second order susceptibility $\chi^{(2)}$. It is therefore important in order to have a high electrooptical coefficient to have a high $\chi^{(2)}$.

We have choosen to use a polar donor-acceptor rigid core as a pending group for the comb-like polymers or copolymers. Figure 3 summarizes the necessary mechanism to obtain a high $\chi^{(2)}$ coefficient with a polar donor acceptor group. The general effect of a strong optical field on a molecule can be considered classically at two levels.[4,5,6]

At the first level the optical field induces a molecular polarization μ ; at the second level the field induced a macroscopic polarization P with $\chi^{(2)}$ and $\chi^{(3)}$ the second and third order susceptibilities. As $\chi^{(2)}$ is a tensor, it is necessary for the system to be non centro-symmetric in order to obtain $\chi^{(2)} \neq 0$. d_{33} is the largest bulk second order coefficient of the tensor $\chi^{(2)}$. As we have seen there is a relationship between for example the electrooptic coefficient r_{33} and d_{33}.

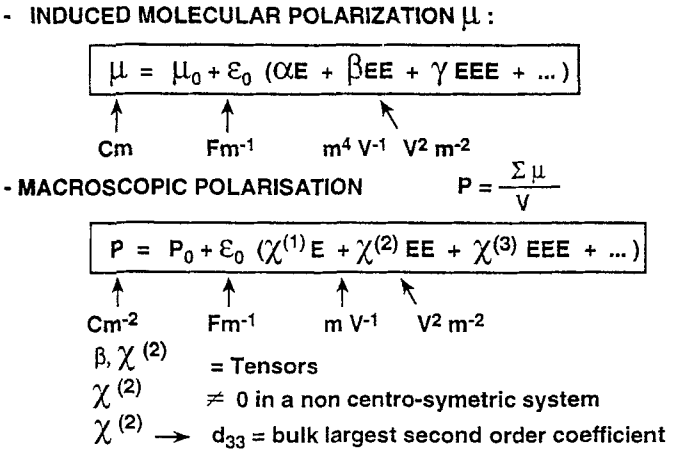


FIGURE 3 Response of a dielectric to a strong optical field

The general formula of these polymers is represented Figure 4, where the NLO unit, used as pending group is of the general formula :

Donor group / conjugated system / acceptor group

the donor group we have used is a tertiary amine, the acceptor group is the nitro group.

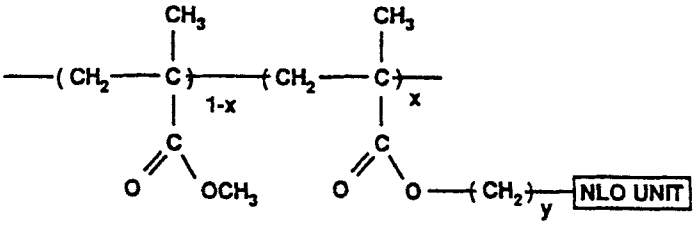


FIGURE 4

The use of polymers in electrooptical components such as modulator seems very interesting when the polymers are soluble because the waveguide layers can be manufactured by spin-coating. Moreover, they have the advantages of organic materials namely :

- high nonlinear coefficients
- fast response time
- high optical damage threshold
- high potential for molecular engineering.

An electrooptic modulator defined as a waveguide structure can be characterized by four principal criteria : modulating voltage, bandwidth, power requirement and propagation losses. The modulator[7] we have made is represented Figure 5.

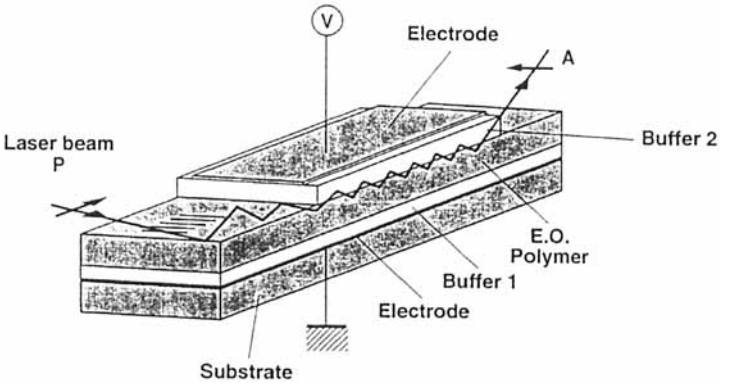


FIGURE 5 Polymer electrooptic modulator

The active NLO polymer is sandwiched between two low refractive index buffer polymers and two electrodes. The modulating voltage $V\pi$ is a function of the electrooptic coefficient r_{33} and r_{13} and is given by :

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

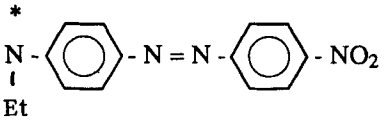
(e = thickness, l = length, n = refractive index, λ = wavelength)

- bandwith : the polymers have a potentially high bandwidth due to their electron mobility. They probably can reach several GHz with an adapted electrode configuration.

- power requirement : low

- propagation losses : the limit of transparency in polymers is known as some 200 dB/km in optical fibers. We have currently obtained one dB/cm with optimized polymers of the polymethacrylate series which we have used with NLO units:

a)  at 633 nm (y = 3)

b)  at 1320 nm (y = 2)

We have obtained for a) r_{33} = 7 pm/V and b) r_{33} = 10 pm/V for $V\pi$ = 13 or 20 V respectively.

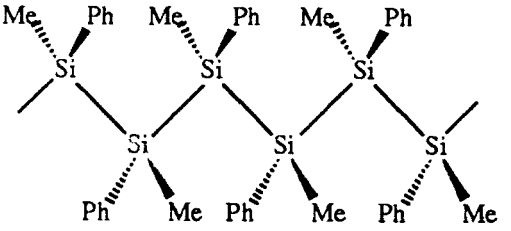
The buffer layers are fluorinated polymer methacrylate derivatives of low refractive index. The life-time of the modulator at room temperature is acceptable without crosslinking of the NLO polymer.

POLYSILANES AND SPATIAL LIGHT MODULATOR

An other example is the association of a photoconductive polymer and a liquid crystal cell to form a component for pattern recognition called a "spatial light modulator" (SLM). SLM's based on the photoconductor - liquid crystal structure are widely investigated.[8,9]. One of the main goals is to achieve high resolution which requires the photoconductor to have a low thickness and a high source-level resistivity.

The polymeric photoconductor

Polymeric photoconductors are interesting candidate.[5] Classical photoconducting polymers are doped polyvinyl carbazole. Recently, polysilanes have been synthesized. However a dopant is necessary to enhance the sensitivity for visible wavelengths since the polysilane only absorbs in the 300 - 400 nm region. The polysilane is the polyphenyl methyl silane :



This compound[10] is synthesised by polycondensation of the dichloromethyl phenyl silane in the presence of sodium using ultrasonic stiring. We have obtained a Tg of 120°C and a molecular weight of $\approx 10^5$. The polysilane is photosensitized by 10 - 30 % of substituted phtalocyanine (Figure 6).

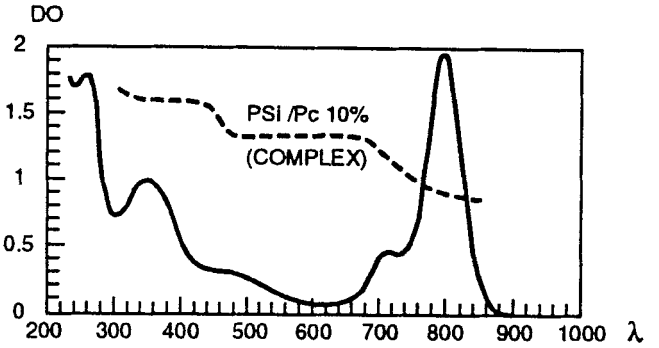


FIGURE 6 Absorption spectra of the phtalocyanine and the complex Psi phtalocyanine (C = 0,22 10^{-5} mol/C - $CHCl_3$)

The liquid crystal cell

The liquid crystal cell associated with the photoconductor is represented Figure 7. The nematic liquid crystal is sandwiched between two ITO electrode with the polysilane on one side. The planar orientation of the liquid crystal is obtained using a polyimide polymer. The liquid crystal is a Merck 3651 chosen for its low dielectric anisotropy and its high resistivity ($\rho > 10^{12}$ Ω.cm).

The writing beam projects the hologram (Fourier transform) of an unknown pattern U and of a reference set S through a writing lens. The interferences of U and S are written by a writing beam (Yag laser - $\lambda = 532$ nm).

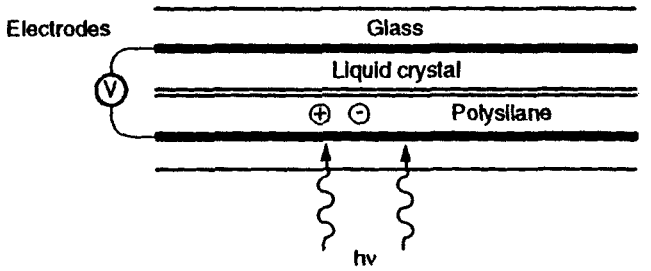


FIGURE 7 Psi / liquid crystal spatial light modulator

The interferences are transferred to the liquid crystal and read by a plane wave (λ = 633 nm). The reverse Fourier transform is obtained by a second lens and allow to obtain the correlation function U x S, when the unknown object is identical to one object of the set. A spatial resolution of less than 10 µm can be obtained for a diffraction yield of 5 %.

The SLM allow pattern recognition with good accuracy of unknown object among a set of known objects.

FERROELECTRIC POLYMERS AND IR IMAGING

Copolymers of the vinylidene difluoride and the trifluoroethylene show interesting ferroelectric and pyroelectric properties[11] :

$$(-CH_2 - CF_2 -)_x \ (CHF - CF_2)_{1-x}$$

They are soluble in solvent such as n-methyl pyrrolidone so they can be spun coated in thin layers on substrates such as silicon. They can crystallise directly in the ß phase which is the ferroelectric phase, depending on the concentration of the co-monomers.

The phase diagram Figure 8 shows the existence of the ferroelectric phase versus the proportions of co-monomer vinylidene difluoride with trifluoroethylene. The ferroelectric phase exists at about 50 % of VF_2. However the most interesting copolymer is around 70 % of VF_2. For x = 0.75, the Curie temperature is around 125°C. In order to obtain the ferroelectric properties it is necessary to polarise the ß non centro-symmetric phase. The applied electric field is in the range of 100 V/µm. For $P(VDF_{75}/TrFE_{25})$ it gives a remanent polarization $P_r = 0.09$ C/m².

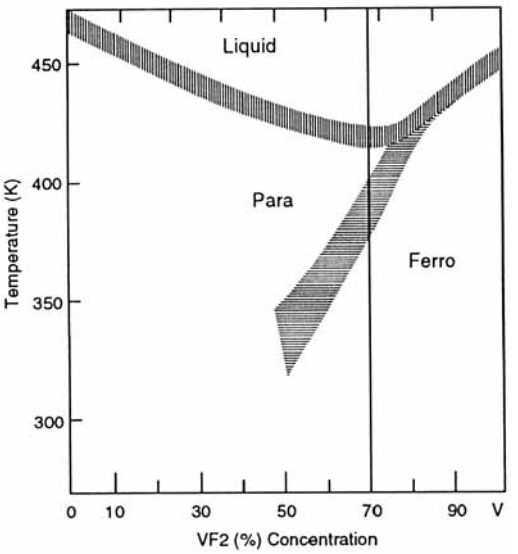


FIGURE 8 Phase diagram of P(VDF-TrFE) copolymers

These ferroelectric copolymers are also pyroelectric. This means that a capacitor formed with the polymer will get a charge proportional to the temperature increase of the material. The measurement of the voltage of the capacitor or of the charge on the electrodes allows the temperature rise of the capacitor and thus the incident IR flux to be determined.

The pyroelectric coefficient is :

$$Py\ (C/m^2/K) = \Delta P/\Delta T$$

This coefficient depends on two factors : the variation of spontaneous polarisation in the crystalline phase (major effect) and the thermal dilatation of the polymers. These two factors are significant in determining the signal to noise ratio of the pyroelectric capacitor - multiplexor couple. Among the different materials which have been studied only the copolymer is directly compatible with the semiconductor fabrication process. The copolymer also shows a low thermal diffusion and the best merit factor (Figure 9). These copolymers are manufactured by Penwalt-Atochem, Kureha and Piezotech.

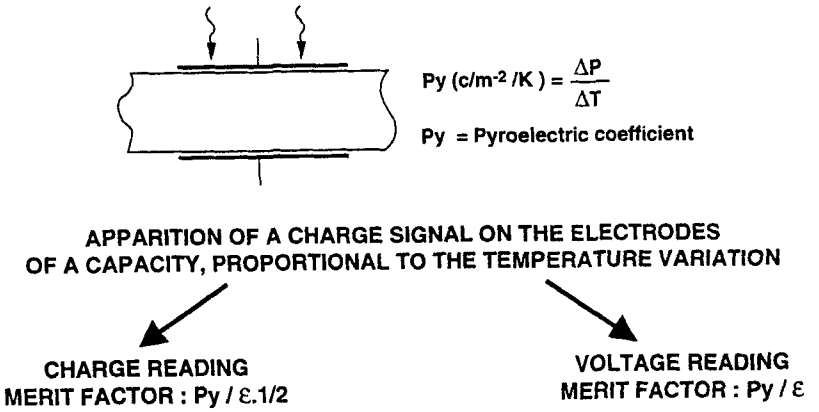


FIGURE 9 Pyroelectricity : principe of the pyroelectricity detection

Thomson-TCS and LCR have realized an IR detector (8 - 14 μm range) associating this copolymer with a silicon CCD matrix.[12,13,14]

The matrix array detector has 128 x 128 pixels of 80 x 80 μm^2 surface area. The NETD (Noise Equivalent Temperature Detection) is 0.64 K at 40 Hz for an f/1 aperture.

One of the advantages of the pyroelectric detector concerns its use at room temperature, as semiconductor detectors work at low temperature. The other concerns its potential low cost.

Applications can be found in different domains such as :

- security (night vision)
- vision through smoke
- anticollision car systems.

POLYMER DISPERSED LIQUID CRYSTALS AND DISPLAYS

Liquid crystal - polymer composites are called Polymer Dispersed Liquid Crystal (PDLC) or Polymer Network Liquid Crystals (PNLC) according to their structure or their method of preparation. These composites have potential applications in the field of displays.

PDLC are formed by droplets of liquid crystal dispersed in a polymer matrix. In the "of" state the micron size droplets, scatter the light ; at the "on" state an electric field is applied so that the liquid crystal is oriented parallel to the field and the composite is transparent if the refractive indices are well adapted.

For this kind of composite a high voltage of 50 V is necessary to address the polymer (30 μm thick).

One of our objectives was to decrease the addressing voltage and keep a good contrast. One of the way is to increase the proportion of liquid crystal ; PNLC are currently obtained with 80 % of liquid crystal in polymers. We have obtained PNLC by photopolymerization of a Merck mixture and obtained a threshold voltage as low as 6 V (see Figure 10). The monomer (Merck PN 350 18.8 %) with the liquid crystal (TL 202) is cured under U.V. (365 nm, 7 mW/cm^2, 16 min). An RC of 240 ms is obtained for this mixture.

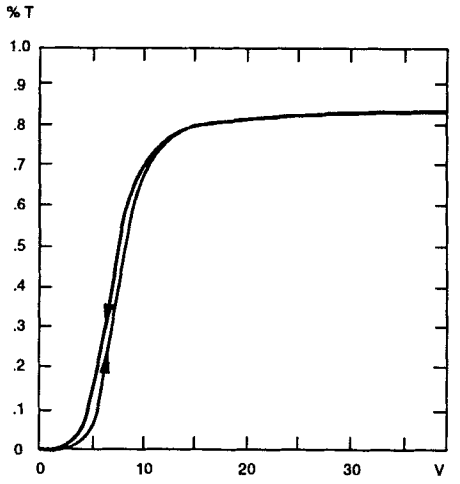


FIGURE 10 Response curve transmission/voltage for a PNLC made by photopolymerisation

CONCLUSION

Organized polymers such as comb like polymers or ferroelectric polymers can be used as active materials in components for electrooptics. The association of these polymers with silicon can conduct to interesting low cost component such as a matrix for IR imaging. Moreover such component is now commercialy available.

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