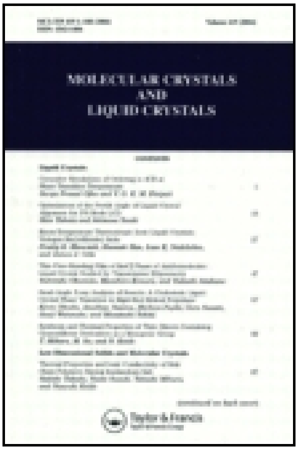

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Laser Written Permanent Gratings in a New Liquid Crystalline Organometallic Polymer

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Laser Written Permanent Gratings in a New Liquid Crystalline Organometallic Polymer

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Interest in materials for optical storage effect has been intense in the last years. In this paper we report the observation of permanent gratings in a new liquid crystalline side-chain polymer containing a mononuclear cyclopalladated azobenzene complex. Two-beam coupling experiments indicate photorefractive properties. A gain of 900 cm^{-1}, without applied electric field, was determined by two beam coupling measurements. A significant feature of this high gain material is that this effect occurs in an easily processable pure compound.

Keywords: optical storage; photorefractivity; metallomesogenic polymers

It has been recently proved that polymers, appropriately doped[1] or containing transition metal complexes as photosensitizer[2], show optical storage due to photorefractive (PR) effect. On the other hand it is known that liquid crystals are suitable matrices for PR composites[3-5], hence, metallomesogenic polymers which combine their mesomorphic nature with a proper metal center, can be expected to form a new class of one component PR materials.

We are currently active in researches on metallomesogens[6] and about such a topic we have synthesized a side-chain polyacrylate incorporating a mononuclear cyclopalladated azobenzene complex[7]. This polymer (fig.1) displays a glass transition at 69°C and above this temperature it give rise to a smectic A mesophase which is stable until 115°C where the isotropic fluid appears. In this paper we report the observation of an optical storage effect. In particular we study the permanent grating formation in a thin film of the material and we performed some preliminary measurement to understand the nature of this optical storage effect.

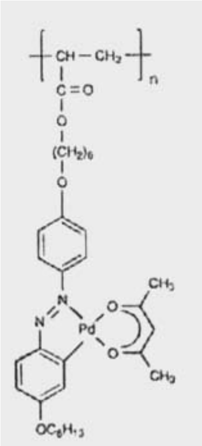

FIGURE 1 Chemical structure of the metallomesogen polymer.

These persistent gratings are obtained using the standard experimental setup[8] for nonlinear grating observations (fig. 2). Two linearly polarized cw Ar^+ laser beams (λ=514.5nm) cross on the sample nearly at normal incidence. An intensity pattern $I \approx I_0[1+\cos(\bar{q}\cdot\bar{x})]$ is produced, being q the grating wave vector, $\Lambda = 2\pi/|q| = \lambda/[2sin(\theta/2)]$ the grating period and λ the light wavelength. The sample used is a film 5μm thick obtained heating the material, placed between two glass plates, at the isotropic phase and then slowly cooling down. Measurements have been taken at room temperature (T=25°).

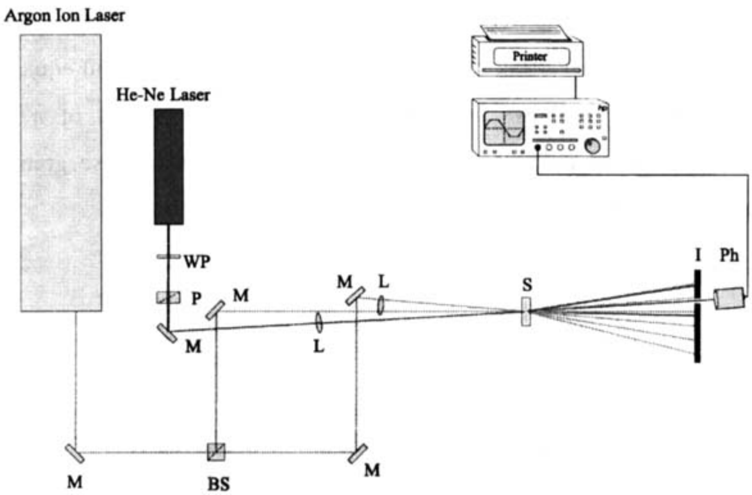

FIGURE 2 Experimental setup for permanent grating writing. WP=wave plate, P=polarizer, M=mirror, L=lens, BS=beam splitter, I=iris, Ph=photodiode, S=sample.

The laser beams intensity required to write these structures is ~50 W/cm^2 for few seconds exposure time. The produced gratings are probed by a polarized He-Ne laser beam (λ=632.8nm) which is diffracted passing through the irradiated area. In order to investigate the gratings, measurements of the diffraction efficiency have been performed. A generally used definition of the efficiency is the ratio $\eta=I_l/I_{inc}$, where I_l is the first diffracted beam intensity and I_{inc} the incident intensity. The diffraction efficiency can be written as[9]:

$$\eta=\left(\frac{\pi\Delta nd}{\lambda}\right)^2+\left(\frac{\Delta Kd}{4}\right)^2 \tag{1}$$

where Δn is the refractive index modulation and ΔK is the modulation of the absorption coefficient. Measurements have been taken both for s and p probe beam polarization and writing beams intensities. The efficiencies values obtained are $\eta_s = 2.4\cdot10^{-3}$ and $\eta_p = 2.6\cdot10^{-3}$ for 5 seconds exposure time at 70 W/cm^2 writing beams intensity with s polarisation and grating constant

Λ=10μm. η_s and η_p values are similar for both s and p writing beams polarisation. Considering a pure phase grating, we obtain from equation (1) $\Delta n \sim 2 \cdot 10^{-3}$. Fig.3 shows an optical microscope observation of a grating between crossed polarisers; this observation indicates a phase grating. No degradation of the grating was observed after several months.

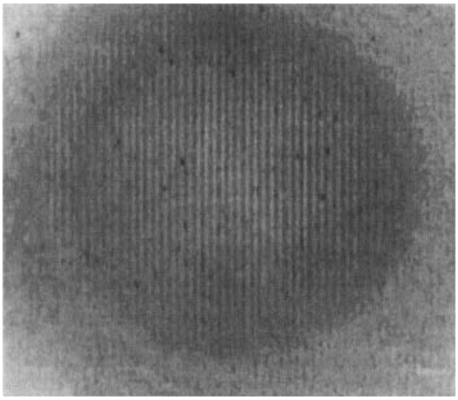

FIGURE 3 Optical microscope picture of a permanent grating, Λ=10μm.

To determinate the nature of the grating, two-beam coupling (TBC) measurements have been done. In the TBC experimental geometry (fig.4), the two writing beams (λ=514.5nm) with a crossing angle θ=6° are directed onto the sample which is tilted at an angle α=30° with respect to the bisector of the writing beams. In this experimental condition only one order of diffraction is observed. The measurements have been taken by chopping one of the two incident beams and detecting the transmitted intensity of the other beam at room temperature without external electric field. In fig.5a we report the transmitted intensity of the beam 2 chopping the beam 1 and in fig.5b the transmitted intensity of the beam 1 chopping the beam 2.

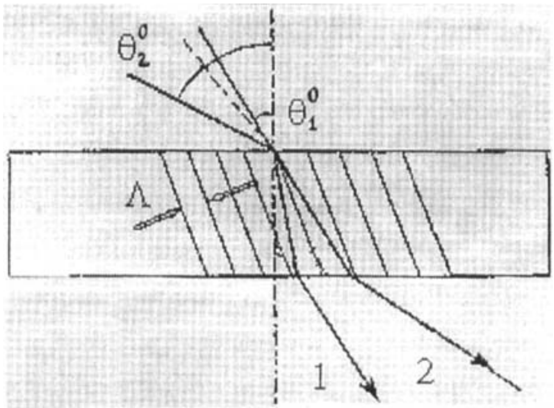

FIGURE 4 Experimental geometry for two-beam coupling measurements.

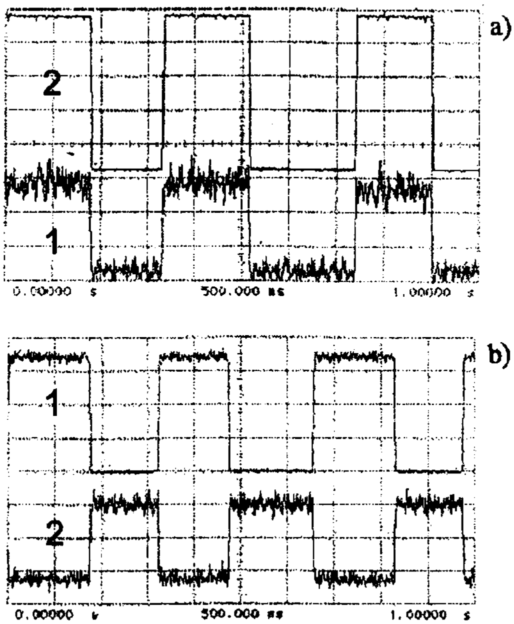

FIGURE 5 Asymmetric energy transfer in the two-beam coupling experiment: a) the beam 1 gains energy; b) the beam 2 lost energy. The top trace shows the chopped pump beam and the lower one indicates the signal beam.

An asymmetric energy transfer between the two beams is evident: one beam gains energy fig.5a while the other lost energy fig.5b. The results of TBC experiments should indicate the photorefractive nature of the observed gratings. In fact the asymmetric energy transfer characterizes this effect due to the non-locality of the photorefractive effect: the refractive index grating is phase-shifted respect to the light interference pattern. A two beam coupling ratio, $\gamma_0 = P_{(\text{signal, with pump})}/P_{(\text{signal, without pump})}$, of 1.33 has been measured for this material. The normalized two beam coupling gain coefficient could be calculated in terms of the measured quantities γ_0 and β (the intensity ratio of the two incident beams)[1]:

$$\Gamma = \frac{1}{L}\left[\ln(\gamma_0\beta) - \ln(\beta + 1 - \gamma_0)\right] \tag{2}$$

where $L=[d/\cos(\alpha \pm \theta/2)]$ is the optical path for the beam with gain. A large gain coefficient, $\Gamma \sim 900\ cm^{-1}$, has been calculated from equation (2) with $L \sim 6\mu m$, $\gamma_0=1.33$ and $\beta=0.55$. This last result is particularly relevant; in fact, the values of two-beam coupling gain coefficient measured with an applied electric field in polymeric and liquid crystalline materials[1-5,10] are one or two order of magnitude lower.

In conclusion a new type of liquid crystalline polymer has been synthesized and characterized for optical storage applications. In this material it has been observed the formation of permanent gratings with a brief exposure time (1-5sec) of two interfering laser beam. These structures are very stable for long time (1 year). The optical storage effect seems to derive from the photorefractive nature of the material as indicated by the TBC experimental results. The TBC gain coefficient measured without any external electric field is much larger than the others found for polymeric and liquid crystalline materials.

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