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Physico-chemical Characterization of 4-(4-Pentenyloxy)Benzonitrile

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Synthesis of photorefractive materials has become an active research area due to their potential use in the manufacturing of electro-optical devices. It is known that substances containing chromophores in general present NonLinear Optical (NLO) properties. We have investigated the NLO properties and self-interaction of laser beam in a medium (due to changes in optical properties of the medium induced by the incident radiation) of a molecule with terminal cyano group. Self-diffraction is produced in non-linear media when the beam power is high enough and has been reported in liquids crystals, organic dyes and polymers. In this work, we present the patterns obtained from 4-(4-pentenyloxy)benzonitrile as a function of the intensity of the incident beam. We studied the self-organization. This material also was characterized by Micro-Raman, DSC, fluorescence and optical techniques.

Keywords: interference; nonlinear optics; self-diffraction

*Undergraduate Student.

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INTRODUCTION

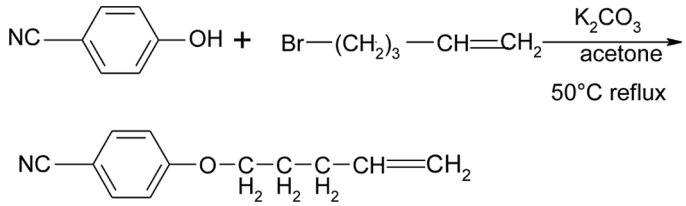
The synthesis of materials has become an active research area due to the potential use of these materials in electro-optical devices. Usually, materials with a terminal cyano group are strongly polar nematic compounds with positive dielectric anisotropy and display a twisted effect. Is widely known that a compound containing cromophores present nonlinear optical properties. Self-interaction of laser beam in a medium is due to changes in optical properties of the medium induced by the incident radiation. Self-diffraction is a very general effect that is produced in non-linear media when the beam power is high enough. Self-diffraction in liquids crystals [1], organic dyes [2,3] and polymers [4] has been reported. On the other hand, self-organized patterns were presented in several reports [5–8]. Many studies exist about solid materials but liquid materials are a good medium to obtain optically-controlled patterns, as well. We implemented an optical arrangement to study the optical patterns formed by self-diffraction and Fabry-Perot effects. Results of characterization of the 4(4-pentenyloxy) benzonitrile by Raman, Micro-Raman, and Differential Scanning Calorimetry (DSC) techniques, and we will study the patterns formed by self-diffraction of the beam and by Fabry-Perot interferometer.

EXPERIMENTAL

Materials and Techniques. Most chemicals were purchased from Aldrich Chemical Co. (Toluca, Mexico) and used as-received. Raman spectra were recorded on a Nicolet Raman 90 spectrometer and an Olympus B × 40 (Dilor) spectrometer. Luminescence information was obtained from a Perkin-Elmer LS-SB luminescence spectrometer. DSC was obtained on Metter Toledo Star System using an isotherm at −10°C by 2 minutes, heating from −10°C to 300°C, cooling from 300°C at 0°C and heating to 300°C, all at a 20°C/min rate. Refraction index was obtained on a Abbe refractometer Erma at 23.3°C. For the optical characterization we used an Argon laser with variable power (514 nm), lens and CCD camera.

RESULTS AND DISCUSSION

4(4-pentenyloxy)benzonitrile ester has been reported to show photo rearrangements under 313 nm irradiation in acetone and 254 nm in acetronitrile [9] and was prepared by standard substitution chemistry. The method to prepare it was described by Subramaniam [10]. We synthesized the ester and reported characterization results.



SCHEME 1 Route of synthesis of 4(4-pentenyloxy)benzonitrile.

Synthesis 4-(4-pentenyloxy)benzonitrile. A mixture of 4-cyanophenol (24.8 g, 0.2 mol), 5-bromo-1-pentene (25 g, 0.17 mol), acetone (200 mL), and anhydrous potassium carbonate (35.5 g, 0.25 mol) was refluxed for 24 h under mechanical stirring at 50°C. The reaction mixture was poured into water, the acetone removed, and the aqueous layer extracted with ether (40 mL, 4X). The ether layer was washed with aqueous potassium hydroxide (2M, 70 mL, 7X), water (40 mL, 4X), and saturated brine (20 mL, 2X) and then dried using anhydrous sodium sulfate (10 g). Removal of the ether gave pale yellow oil, which was purified by distillation at a reduced pressure (see Scheme 1). Yield 60%. IR (neat) 2223, 1605, 1508, 1258, 1171, 916, 834, 704, 548 cm^{-1}. ^1H NMR ($CDCL_3$): δ 7.59-6.88 (d de t, AA 'BB', 4 H, aromatic), 5.81, 5.10-4.97 (m, 3 H, -vinyl), 4.00 (t, 2 H, $-OCH_2$), 2.24, 1.89 (m, 4 H, $-CH_2CH_2$). ^{13}C NMR ($CDCL_3$): δ 119.23 (CN), 103.69 (NC−C, aromatic), 133.90 (=C−, aromatic), 115.12 (−C=, aromatic), 162.30 (C−O, aromatic), 67.45 (O−CH_2), 28.03, 29.88, (CH_2−CH_2), 137.28 (CH), 115.50 (CH_2). APT: UP (CN, NC−C,C−O, O−C, CH2), DOWN (CH). The corresponding refraction index is 1.534.

The Raman spectrum [11] (Fig. 1a) was obtained in liquid state and presents peaks at 3070.10 nm (CH ring), 2217.74 nm (CN), 1597.68 nm (1,4 benzene), 1636.58 nm (vinyl), 1165.20 nm (6-ring), 829.42 nm (1,4 benzene), 642.16 and 474.27 nm (C−O−C). The Micro-Raman Spectrum (Fig. 1b) showed peaks at 1156.22 and 1592 nm (ring benzene), 2212.22 nm (CN), 3070 nm (CH, ring), we saw that it had fluoresce at 655 nm. The emission spectrum at 655 nm showed a maximum exited wavelength at 334 nm.

The DSC thermogram (Fig. 2) shows three signals; in the isotherm one can observe the crystallization point of the liquid at −9.93°C ($\Delta H = 77.8$ J/g), to obtain this it was necessary use an isotherm. Upon first heating, a melting point at 4.6°C ($\Delta H = -75.5$ J/g) and finally the boiling point at 306.8°C ($\Delta H = -393.1$ J/g) were present. Upon cooling and second heating it is not possible to observe the signals because the compound was evaporated or decomposed during the first heating.

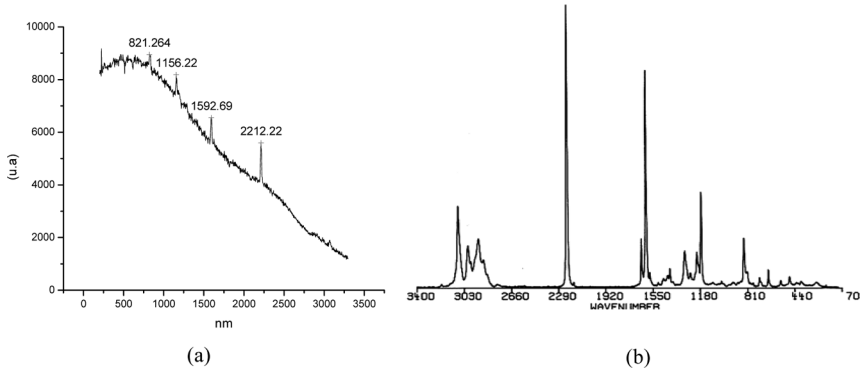


FIGURE 1 Raman and Micro-Raman spectrum of 4-(4-pentenyloxy)benzonitrile.

This is important because at high temperatures up to 300°C it will not be possible to analyze the material by some thermal techniques, but by using optical techniques it is possible to obtain additional information about their optical properties.

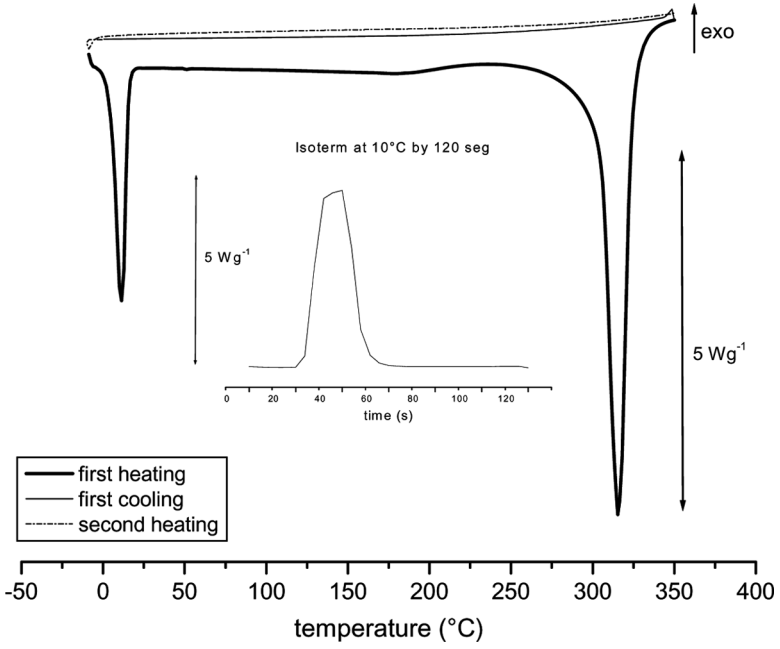


FIGURE 2 DSC Thermogram.

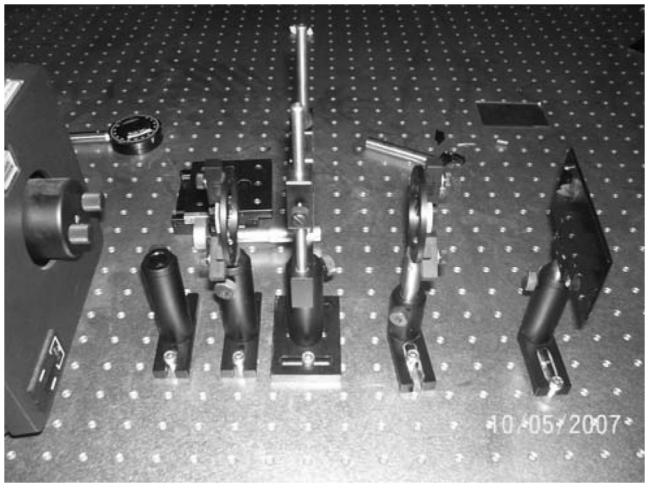


FIGURE 3 Optical arrange to produce the patterns.

Self-diffraction patterns are characteristic properties of nonlinear optical materials and are formed due to the nonlinear refraction index, depend on the beam power. Changes in refraction index can be due to electronic effects or to changes in temperature. The Fabry-Perot effect is known and it is formed by a plane parallel plate; when the beam is reflected multiples times [12]. We use a cell (2 mm) with a 4-(4-pentenyloxy)benzonitrile compound in liquid state to generate the self-diffraction pattern and the Fabry-Perot pattern are present and analyzed changes that occur when the beam power is increased. The optical arrange is show in Figure 3.

Laser beam travels through a lens (50 mm) and the input face of cell is at the focus, output face is focused with another lens (75 mm) and the image is captured by a CCD camera. The power of the incident beam was increased from 200 mW to 2500 mW and the image was captured, after being attenuated conveniently by a filter to avoid a saturation signal in CCD, without moving any other arrange element. Some images obtained are shown in Figure 4 with different powers.

The image at 200 mW shows the spot of beam with some deformation, at 400 mW it is possible to see the self-diffraction pattern characteristic of non lineal materials, in this pictures the Fabry-Perot do not present an interference because the intensity of the beam is not enough but up to 1000 mW this effect is observable. Notice the beam deformation at 1500 mW, the pattern begins to form many spots and it is symmetric with respect to the y axis, when the intensity is

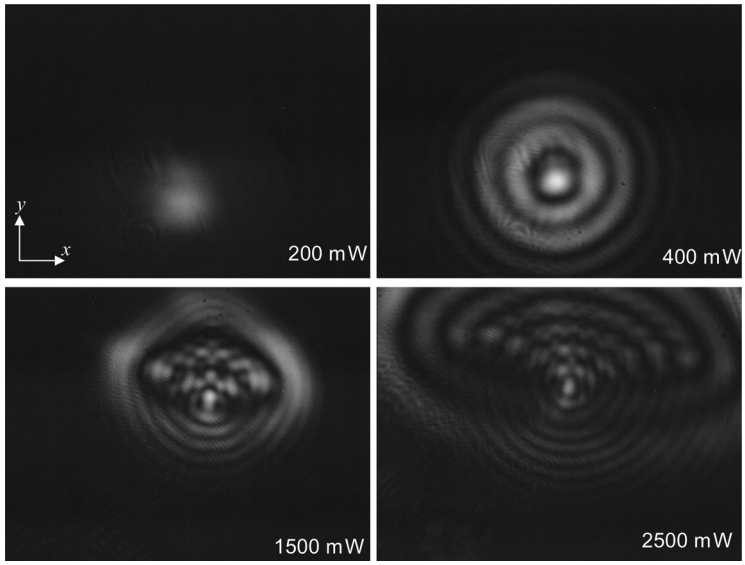


FIGURE 4 Images obtained by CCD at different power of laser.

increased the number of spots increases too, it can observed in picture at 2500 mw where they are organized having a "Y"-shaped curve. This pattern is formed by the interaction of two Fabry-Perot patterns as it is shown in Figure 5. Notice that there exist two patterns of bright spots arranged with a "Y" curve form. Nevertheless, there are other

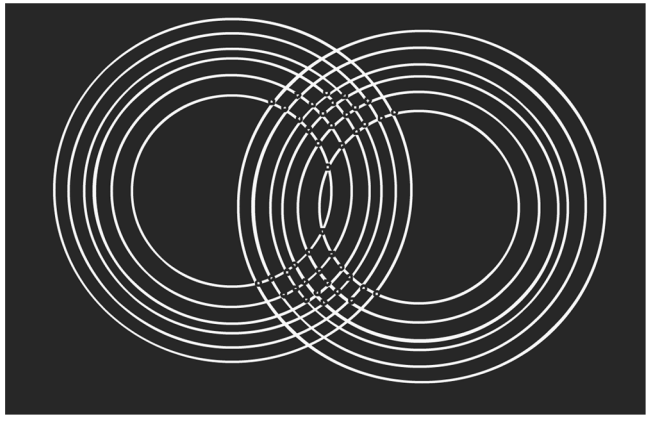


FIGURE 5 Scheme shown the interference of two Pabry-Perot patterns.

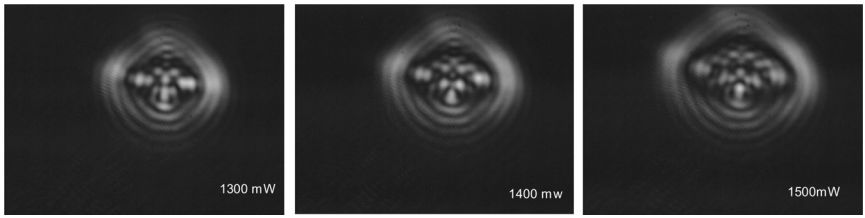


FIGURE 6 Develop of spots versus increased power of beam.

possible explanations which require further experimentation, currently under way.

When the intensity of the beam is increased in a nonlinear optical material, the phase of the beam changes due to a self-phase modulation effect, then the self-diffraction pattern is dynamic. Nonlinear optic effects allow energy transmission from their central spot to other spots. Figure 6 shows the development of spots formation while the intensity is increased from 1300 to 1500 mW, notice the increase of spots number is a nonlinear function of the intensity, the central spot is broken into transfer energy to the interference pattern and the spots can be seen while energy is transferred.

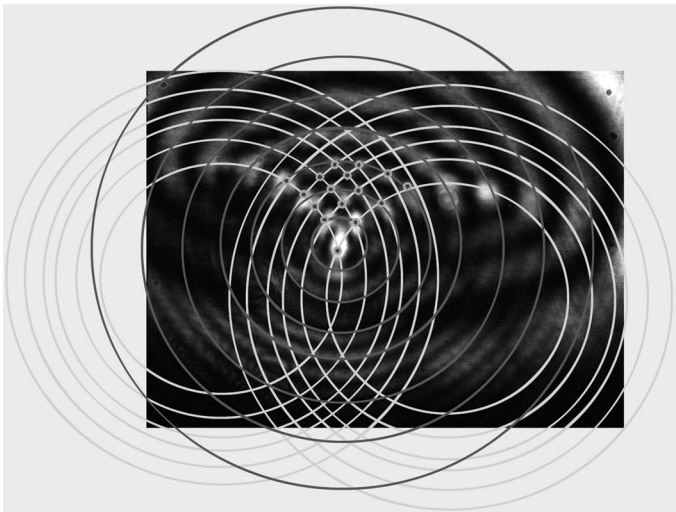


FIGURE 7 Draw of self-diffraction and Fabry-Perot patterns over the photograph.

Figures 4 and 6 show only spots arranged in the upper part, this is because only the energy of the central spot can be transfered to the neighboring closed interference points. This is due to the fact that self-diffraction pattern forms an isosceles triangle with the two Fabry-Perot patterns, and the closed points are the upper, this is shown, in a drawing over the picture in Figure 7. However it is not possible to observe the Fabry-Perot patterns in the experimental picture (Fig. 4) due to their intensity which is less than self-diffraction pattern.

CONCLUSIONS

DSC, Micro-Raman and Raman characterization of 4(4-pentenyloxy)-benzonitrile were presented. This material is fluorescent when excited to 334 nm. With the arrangement it is possible to have control over the interaction between patterns formed by self-diffraction effect, and Fabry-Perot interferometry patterns. This effect can be used in optical devices to design multiplexors.

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