Optical and thermal properties of luminescent organic-inorganic hybrids

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Abstract

In this work, the NLO properties of organic-inorganic hybrid materials based on 4-[[5-dichloromethylsilyl]pentyl]oxy]-cyanobenzene (DCN) and tetraethoxysilane (TEOS) were investigated. Luminescent hybrids were produced by the sol-gel process from a dicholorosylane and TEOS. Nature of self-diffraction patterns, obtained after irradiating samples with an Argon laser, are discussed. Finally, the thermal properties of hybrids obtained by differential scanning calorimetry (DSC) are explained in terms of crosslinking reactions and morphology.

Introduction

Synthesis of photorefractive materials has become an active research area because of their potential use in the fabrication of electrooptical devices. Usually, molecules that exhibit a liquid crystalline behavior with a terminal cyano and nitro groups are strongly polar nematic compounds. They also have positive dielectric anisotropy and display a twisted effect. It is known that substances containing cromophores present nonlinear optical (NLO) properties too.

Self-diffraction is a general effect produced in a non-linear media provided the beam power is high enough. Observation of this phenomenon has been reported in liquids crystals [3], organic dyes [4, 5] and polymers [6]. The self-interaction of a laser beam in a medium is due to changes in optical properties of the medium, induced by the incident radiation. In this work, self-diffraction studies observed on hybrid organic-inorganic materials when they are irradiated with a CW Ar ion laser are presented. Analysis of the interference rings evolution due to changes by the incident radiation in the hybrid material is discussed.

Experimental

Samples were prepared from 4-[[5-dichloromethylsilyl]pentyl]oxy]-cyanobenzene (DCN) and TEOS by the sol-gel technique, as describe elsewhere [8]. Different molar ratios were used to prepare the hybrids. Hybrid A was obtained from a TEOS/DCN:HNO_3 molar ratio of 1/0.3:(0.3% vol). For hybrid B, a TEOS/DCN:HNO_3 molar ratio of 1/0.7:(3% vol) was used. A CW Ar-ion laser at 514 nm with variable power was employed to study the patterns formed in far field conditions. The experimental setup is shown in Figure 1. Analysis by DSC was performed on a Meter Toledo Star DSC 820e calorimeter previously calibrated with indium. DSC analysis of

the samples was made as follows: Hybrids and oligomers were heated at 10°C/min from 0°C to T_{max} and cooled at the same rate to T_{min} and again heated to T_{max}. The glass transition temperature was calculated at the midpoint of the heat capacity change.

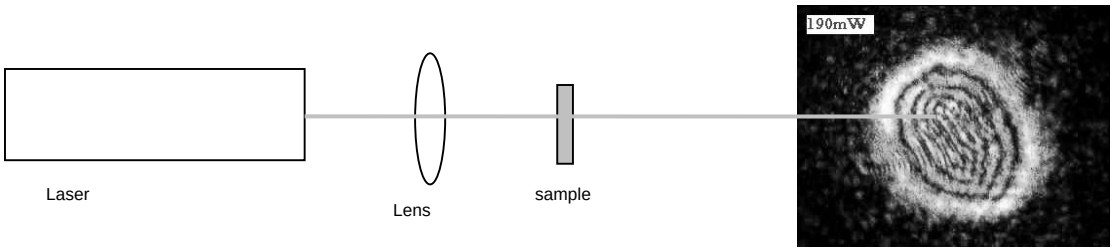

Figure 1. Experimental setup for the optical analysis

Results and discussion

Self-diffraction patterns with an elliptic form for different intensities applied to samples of hybrid B were obtained (Figure 2).

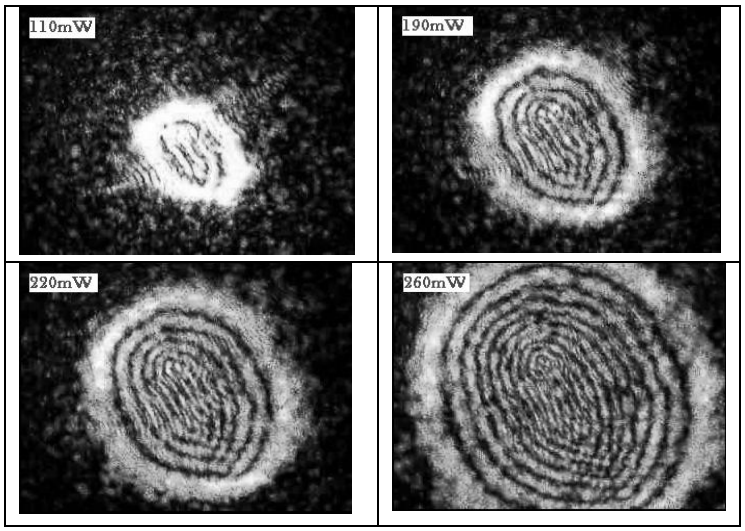

Figure 2. Self-diffraction pattern of the hybrid materials to different power of laser

It was found that there is a dependence of the number of ring with the laser intensity [9]. The thermograms in figure 3a, show a wide endothermic peak (10.6-175°C), centered at 85°C (ΔH =66.6 J/g,) for hybrid A. Within this temperature range, dehydration reactions that lead to crosslinking occurred. A broad peak is also present in the thermogram for hybrid B (4.6°C- 217°C, ΔH = 7.3 J/g), but this has lower intensity. Wide peaks in both hybrids could be attributed to the chemical reactions between hydroxyl groups to form Si-O-Si bonds (crosslinking). For hybrid B, within this temperature range, other peak at 112.7°C (ΔH = 1 J/g) due to the formation of linear copolymer formed by DCN units and TEOs hydrolyzed is observed. For hybrid A, small exothermic peaks at 52.8° and 55.8°C (ΔH =0.47 J/g), due to the presence of some cyclic oligomers and cyclic D_nQ_m copolymer formed respectively, are also seen. Notice the absence of these signals in the thermogram for hybrid B, which indicates that formation of cyclic units is not favored under the reaction conditions used. During cooling (figure 3b), three signals can also be observed in hybrid A: one exothermic peak centered at 101° C (ΔH = 0.003 J/g), which correspond to crystallization of linear copolymer, and two endothermic peaks centered at 30° C (ΔH = 0.11 J/g) and at 21.9° C (ΔH = 0.051J/g), due to crystallization of cyclic oligomers and cyclic copolymers. In thermogram for hybrid B, an exothermic signal due to crystallization of linear copolymer units at 99.1° C (ΔH = 0.5 J/g) is observed.

During the second heating, two signals are observed for hybrid A: one at 52° C (ΔH =0.5 J/g) that correspond to the exothermic process of crystallization of cyclic oligomers and cyclic copolymers, and a wide signal centered at 116° C (ΔH =3.9 J/g) due to dehydration reactions that led to crosslinking and linear copolymer formation. This peak is slightly shifted towards higher temperature. Nature of crosslinking process is different in the second heating, as condensation reactions correspond to remaining hydroxyl groups that do not react during the first heating. In the thermogram for hybrid B, a less intense broad signal is detected. This signal is slightly shifted with respect to that observed during the first heating. This is expected as material morphology has changed after crosslinking. An endothermic signal at 108° C (ΔH = 0.5 J/g), due to linear copolymer, is still present.

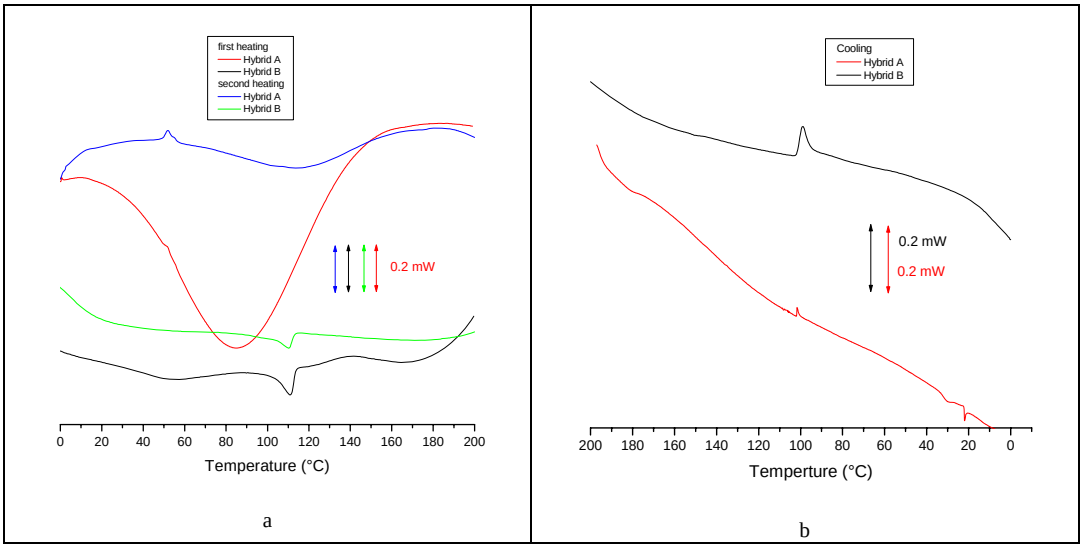

Figure 3. DSC thermograms of Hybrid A and Hybrid B a) heating, b) cooling.

Conclusions

Characterization by two different techniques of inorganic-organic hybrids obtained from DCN and hydrolyzed TEOS was achieved. These materials show thermal stability up to 200° C. Several physical changes and chemical reactions are detected in DSC thermograms, which were assigned based on monomer and oligomers thermograms. The most important signal in the thermogram is a broad peak due to release of water, leading to the formation of crosslinking structure. The self-diffraction effect observed in this material, as concentric elliptic patterns, is mainly due to non-linear absorption. As the sample is exposed to a CW Ar-ion laser beam, the number of rings increases and the visibility of such rings fluctuate with time and intensity of the beam. These hybrid-materials provide systems for the study of nonlinear optical effects at relatively low powers. Therefore, they can be used in the design of optical limiting devices, for optical bistability applications and for other applications proper of NLO materials [10-12]

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