

the bulk generated thermal-wave signal also involved light reflection at void interfaces.

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Iodine-incorporated polystyrene for laser marking

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An iodine-incorporated polymeric film, based on a solid-state charge-transfer complex between polystyrene and iodine, is described. The material prepared, originally red, can be marked (changing to transparent) by an Ar⁺ laser beam. Possible photochemical and photothermal mechanisms for such transformation are proposed. The laser print can be erased by exposing the film to I₂ vapor. Besides its use as a laser-beam diagnostic material, possible future applications include optical storage devices.

Optical storage devices are among the most important components for the development of a variety of modern branches of industry, including computers, office instruments, amusement equipments, etc. The main reasons for this are the possibilities of a high density of storage and fast laser writing and reading techniques. All types of optical memories are based primarily on the same basic principle: they use the change in optical properties of a surface or thin film to modulate a laser beam. This modulation is then read as an on/off signal. Therefore, there is an ever increasing search for materials which can have their optical properties changed by special light (lasers) or particle (electron) beams. Much progress has been made in the last few years and the scientific literature is now crowded with examples of various types of optical disks and memory devices.¹ Materials of different molecular basis have been used, in special nematic² and smetic³ liquid crystals and other types of organic molecules,^{4,5} some of them with reversible recording capability.⁵ Advantages and drawbacks exist for each of them, but rapid progress is being made because of their technological importance.

In this communication, we report some recent results on simple polymeric composition films which were made of

normal (atactic) polystyrene (PSt). The resin used was manufactured by a Brazilian supplier (Estireno do Nordeste S.A.) and was free of additives. Good uniform, transparent films were easily produced by casting the material dissolved in carbon tetrachloride or chloroform on a flat, clean substrate surface, the solvent being vaporized out under heat-controlled conditions. After drying, the PSt films were then exposed to iodine (I₂) vapor for the doping process. This step can be performed either at ambient conditions or under vacuum and/or heating. Generally, a 20–40- μ m-thick film would be turned deep red after exposure to I₂ vapor for about 4 h. In order to understand the iodine-polystyrene interaction, visible near ultraviolet absorption spectra of the film were measured from 900 to 190 nm, using a Lambda-3, VIS-UV spectrophotometer from Perkin Elmer. Figure 1 shows the spectra of a pure, 10- μ m-thick PSt film (a) and the same film after doping with I₂ (b). In the pure PSt film strong absorptions are observed below 270 nm. These bands correspond to the known transitions of polystyrene⁶ and involve electronic excitation of the delocalized electrons of the aromatic rings hanging on the main polymer chain. In Fig. 1(b) two new features are apparent; there is a relatively small absorption band between 580 and 420 nm with the minimum

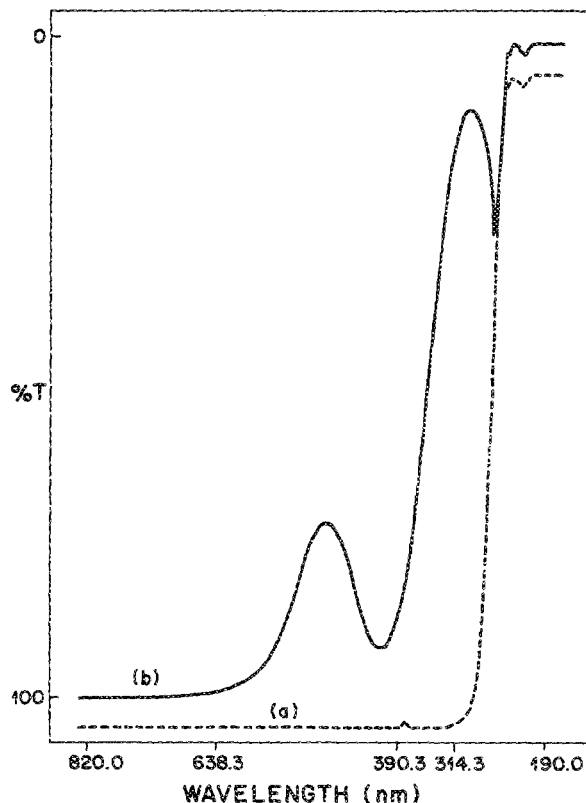


FIG. 1. The absorption spectra of polystyrene films, pure (a) and I_2 -incorporated (b), at ambient conditions. The films present equal transmission at wavelengths greater than about 640.0 nm. The pure polystyrene film spectrum (a) is shifted for a better comparison of relative absorption intensities. The small "peak" close to 390 nm in spectrum (a) is an artifact and corresponds to a change in one of the spectrophotometer filters. In the order of decreasing wavelengths, spectrum (b) shows the molecular I_2 transition at 495 nm, the PSt- I_2 charge-transfer band at 310 nm and the PSt electronic transitions below 270 nm.

transmission at about 495 nm. This is probably responsible for the deep red color of the doped film. There is also a stronger band between 420 and 270 nm with the maximum absorption at about 310 nm. The laser marking capability was tested using the output beam of a cw Ar^+ laser, operating at multiline, with main emissions at 488.0 and 514.5 nm and power levels from 50 mW to 1 W. Exposure times to the laser beam from 1 to 60 s were used. Even at the least favorable condition (exposure at 50 mW for 1 s) a color transformation could be observed, with a change from the red to the transparent in the region of interaction, leaving a clear marked spot with the laser beam shape. Figure 2 illustrates the laser marks for beam power at 500, 300, and 100 mW after 5 s of interaction. A small difference in spot size is observed, the higher power beams leave larger diameter marks. The same marking effect was also observed when cw CO_2 and pulsed XeCl excimer lasers were used. These results will be reported elsewhere.⁷ The marking process is erasable, i.e., the film can regain its original color after exposing again to I_2 vapor.

The mechanism of charge transfer (CT) to iodine has been extensively studied for a long time.⁸ It has recently become of increasing interest because of its role in some special

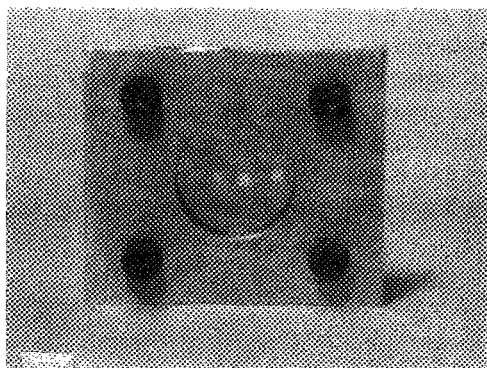


FIG. 2. Illustrating an iodine-doped PSt film marked with Ar^+ laser beams, from left to right (A) 100 mW, (B) 500 mW, (C) 300 mW. Film thickness: 35 μm , mark diameters 1.1–1.7 mm.

polymers doped with iodine,⁹ many of them showing a drastic change in electrical conductivity.¹⁰ A deep understanding of the iodine-polymer interaction is fundamental for describing the conduction mechanism in such systems. Solution charge-transfer complexes have been most deeply analyzed.¹¹ In general, there are two main evidences for inferring the formation of a CT complex in solution for (a) the main absorption band of molecular I_2 in solutions of noninteracting solvents (like CCl_4) is at 520 nm, which tends to shift to the blue with increasing donor concentration,⁸ and (b) a new (generally very strong) band is also present in the UV region and is assigned to CT from the Lewis base (donor) to iodine.⁸ One of the most simple and well-studied cases involves the transfer of aromatic ring delocalized π electrons toward I_2 .^{8,12} A similar type of interaction would be expected for an aromatic electron system in polymer molecules, like polystyrene. The spectrum in Fig. 1(b) seems to indicate a charge-transfer type of interaction between iodine and polystyrene. Since it is a solid-state interaction, the I_2 molecular band exhibits a peak at 495 nm and is shifted by about 25 nm from the CCl_4 solution value (520 nm). The second stronger band at 310 nm seems to be due to PSt-to- I_2 charge transfer, similar to that observed in other systems.⁸ From a qualitative point of view, the Ar^+ laser-induced decoloration in the doped polystyrene film may be attributed to a sequence of elementary processes. First there is a photochemical coupling between the laser and the material due to resonant electronic excitation of the I_2 molecules. Thereafter, two main relaxation channels are possible for the excited species. They may dissociate into kinetically hot I atoms that may then leave the laser-beam region. Predissociation at the $B^3\pi_{0_u^+}$ state of I_2 has actually been observed at wavelengths close to 500 nm.^{13,14} Alternatively, they may transfer their excess electronic energy to the polymer matrix, generating local heat and increasing the sublimation rate of solid iodine at the interaction region. Since our laser is operating at a multiline and the Ar^+ lines have different quantum efficiencies for photodissociation of I_2 ,¹⁴ it is expected that both relaxation channels mentioned above would contribute simultaneously to the final desorption step. However, we do not yet have irrefutable data on the relative importance of them.

Finally, some other aspects of the laser marking capability of our polymeric composition are worth commenting. Based on our preliminary observations, an estimate of the writing speed can be made. We have observed 1.0-mm-diam marks using an Ar^+ laser-beam power of 50 mW and exposure time of 1.0 s. Since an inverse relationship between the minimum exposure time and the laser power fluence (W/cm^2) for a given quality of prints is expected, marks of $10\text{ }\mu\text{m}$ in diameter should be obtained using the same beam power in about $20\text{ }\mu\text{s}$. Again, this would still be dependent on the molecular mechanism of desorption. The iodine-incorporated polystyrene films described in this communication are easy to produce and are inexpensive. They may be useful as a diagnostic means for the shape and the power of laser beams. Besides its sensitivity to the blue-green lines of the Ar^+ laser, recent results have shown that it can also be marked with IR and UV laser light.⁷ The laser marks can be erased by reexposing the film to I_2 vapor. Future possible applications include any optical storage devices. The main disadvantage is the slow but steady loss of iodine through sublimation, if the system is kept in direct contact with the environment. Methods for greater dopant stabilization must be developed before such a film can be used for practical applications. Hopefully, the basic principles and the marking mechanism discussed here may prove helpful in triggering ideas for the design of new optical storage systems. Detailed spectroscop-

ic and electrical properties on similar systems are currently under investigation in our laboratory.

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Ion-induced etching of SiO_2 : The influence of mixing and lattice damage

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Modulated-beam mass spectrometry has been used to investigate the ion-induced etching of SiO_2 in the presence of a flux of XeF_2 . The types of desorbed etch product are characterized. It is also demonstrated directly that mixing leads to an enhanced etch rate while the presence of lattice damage does not produce spontaneous etching. It is concluded that all available data for the etching of SiO_2 with XeF_2 is consistent with the original hypothesis of Y. Y. Tu, T. J. Chuang, and H. F. Winters [*Phys. Rev. B* **23**, 823 (1981)], that the etching reaction is primarily based on a mechanism involving chemical sputtering.

Mayer and co-workers and Dieleman and co-workers have independently suggested that mixing was an important factor for the enhanced etching observed under ion bombardment.¹⁻⁴ Recently, Oostra, Haring, and deVries have made the same suggestion for the etching of SiO_2 under irradiation by argon ions and XeF_2 gas.⁵ The evidence upon which these suggestions are based is somewhat indirect. Therefore, one of the major purposes of the present work was to obtain direct evidence substantiating the importance of mixing. In addition, Oostra and co-workers have reported the presence of etch products which produce the fragment

ions SiOF_2^+ , SiO_2^+ , SiO^+ , Si^+ , and F^+ which were not observed in the original investigation of etch products from this system because of signal-to-noise problems.⁶ Therefore, another purpose of this communication is to support the claim that these fragment ions are present and to suggest a parent molecule. Furthermore, we will also emphasize conclusions about the etch product distribution and show that ion-induced lattice damage does not lead to an enhanced spontaneous etch rate. Finally, it will be suggested that all the data are consistent with the chemical sputtering model originally proposed by Tu, Chuang, and Winters.⁷