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# Laser-induced iodine desorption from impregnated polystyrene

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The  $\text{Ar}^+$  laser-stimulated desorption of iodine molecules from an impregnated polystyrene film was investigated. The photoprocess induces a color change (from red to the transparent) and leaves in the film a marked print, which is related to the laser beam characteristics. The experimental data was fitted using a set of differential equations relating the time dependence of the film temperature and absorption coefficient. At low-power levels ( $< 25$  mW), the time evolution of the laser transmitted power could be well matched to the experimental data. The wavelength dependence of the marking process was also studied and the relative contribution of photodissociative and photothermal processes was inferred.

## I. INTRODUCTION

The study of laser interaction with different materials is a subject of increasing relevance because, besides its intrinsic basic scientific interest, it is related to various technological applications. In particular, understanding how high-power laser beams interact with solids, like metals and plastics, is fundamental for the use of these sources in materials processing. Another application where laser-solid interaction is quite important is in the field of optical recording. The possibilities of a high density of storage and fast laser writing and reading techniques have motivated outstanding efforts in the search for materials that could be marked by laser beams and with which new ideas could be tested. In general, laser recording devices consist of a series of layers of polymers, dyes, and/or a mixture of these on top of a metal substrate. A greater understanding of how lasers of different wavelengths interact with these materials is, therefore, of paramount importance for advancing in the field.

While studying the role of crystallinity on the optical and electrical properties of some polymers, and analyzing the detailed dopant-polymer interaction during and after the impregnation process, we have recently observed what seems to be a charge-transfer complex between polystyrene (PSt) and iodine ( $\text{I}_2$ ).<sup>1</sup> It was also observed that different types of laser sources can induce localized photodesorption of the iodine, leaving a clear memory print that is related to the characteristics of the laser beam, such as the diameter, shape, and power. The scientific interest of these studies is related to the following: (i) PSt: $\text{I}_2$  can be marked by a readily available radiation source such as an  $\text{Ar}^+$  laser. Consequently, it belongs to a technologically promising class of useful laser marking materials, namely, polymers that can be doped by dyes or other light absorbing centers with which the laser interaction can induce a color change. (ii) The  $\text{I}_2$  doping process is extremely simple and cheap. (iii) The understanding of the physical and chemical processes involved in the interaction of the laser with the doped polymers is a subject of considerable scientific and technological interest. In this paper we present a more thorough investigation of the

$\text{Ar}^+$  laser-induced photodesorption of iodine from doped PSt by proposing a physical model that fits the desorption kinetic data and discussing the wavelength dependence and possible mechanisms of desorption.

## II. EXPERIMENTAL RESULTS

Atactic polystyrene (EDN-89 resin from EDN SA, a Brazilian supplier) was first dissolved in chloroform to a 5% (w/v) solution. The films were produced by casting the dissolved material on a clean, flat glass substrate surface and vaporizing out the solvent at about 40 °C inside a laboratory dry oven. The film was separated from the glass substrate by immersing both in a hot water bath ( $T \approx 60$ –80 °C). Pinhole-free, transparent ( $\approx 87\%$  transmission in the visible region), homogeneous films were produced, with thicknesses between 5 and 100  $\mu\text{m}$ . After drying, the film was cut in  $1 \times 3$ -cm pieces for the different experiments.

The iodine impregnation was performed by using either vapor-phase or solution doping. In the first case the casted polymer films was placed inside a closed glass test tube containing a few crystals of iodine at the bottom. When using solution doping, the polystyrene film was immersed into a saturated solution of iodine in methanol (about 23.0 g of solid per 100.0 ml of solvent). In either case, the doped film was then thoroughly rinsed with methanol or isopropyl alcohol before any further handling. This procedure eliminates traces of iodine crystals on the polymer film surface.

Since iodine is known to sublime at ambient pressure and temperature ( $T \approx 23$  °C), we have determined the rate of desorption under these conditions by following the change in absorbance of a vapor-phase impregnated 40- $\mu\text{m}$ -thick film after doping saturation (roughly 20 h). For this step we have used a spectrophotometerlike optical assembly consisting of a 250-W halogen lamp, a PAR model 192 light beam chopper at 15 Hz, a FUNBEC Model UNICROM-100 grating monochromator, and a pyroelectric detector connected to an Ithaco model 393 lock-in amplifier. The monochromator was set at 495.0 nm, which corresponds to the peak absorption of iodine in the charge-transfer complex band system.<sup>1</sup>

The total band width was estimated to be about 100 Å. Figure 1 shows the data taken over a period of 19 days. These results correspond to a decrease to about 30% in absorbance after such a period. The relatively small desorption rate is related to the charge-transfer bonding energy between molecular iodine and the polystyrene aromatic rings.

Next we have conducted thermal desorption measurements using the same optical method. The experiment was performed by leaving a small piece of the doped film for 10 min inside a laboratory dry oven, temperature controlled to within 1 °C. The absorbance was measured after each heating step. The sample was a 167 h vapor-phase impregnated 53-μm-thick film. The solid curve in Fig. 2 represents the data fitting of the absorbance ( $\gamma$ ) data to the theoretical expression predicted by a first-order desorption model.<sup>2-4</sup> In this case, we have assumed that the rate of change of the I<sub>2</sub> concentration (and, consequently, of the absorbance) with respect to the temperature is described by an Arrhenius-type expression, namely,

$$\frac{d\gamma}{dT} = -K_0 e^{-\theta/T} \gamma, \quad (1)$$

where the preexponential factor  $K_0$  and the activation temperature  $\theta$  are characteristics of the materials and depend on the doping process and the doping time. Integrating Eq. (1) with the condition that  $\gamma = \gamma_0$  at  $T = T_0$ ,  $T_0$  being the room temperature (300 K), one gets

$$\gamma = \gamma_0 \exp[-g(T)], \quad (2)$$

where

$$g(T) = K_0 [TE_2(\theta/T) - T_0 E_2(\theta/T_0)]. \quad (3)$$

In Eq. (3),  $E_2(Z)$  is the exponential-integral function.<sup>5</sup> Using the above expression in the data fitting yielded  $\gamma_0 = 2.95$ ,  $K_0 = 1.8 \times 10^5 \text{ K}^{-1}$ , and  $\theta = 5704 \text{ K}$ . The value we got for the activation temperature corresponds to a desorption en-

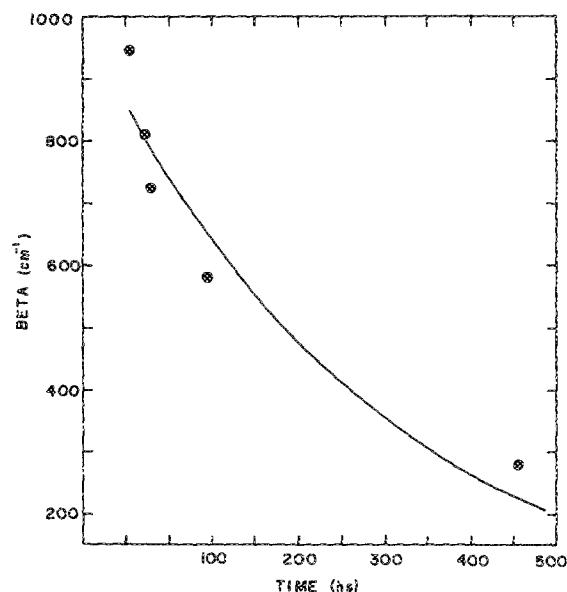


FIG. 1. Absorption coefficient at room temperature for a 40-μm-thick PSt:I<sub>2</sub> film as a function of time. The sample was first left doping for 14 days using the vapor-phase method.

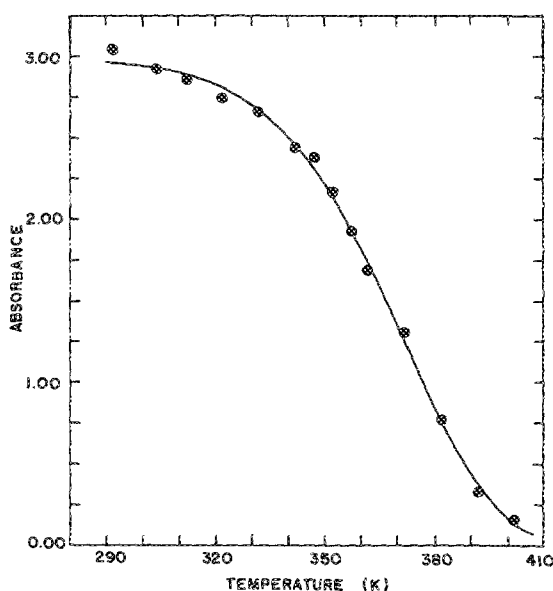


FIG. 2. Absorbance evolution as a function of the temperature for a 167-h vapor-phase-doped, 53-μm-thick PSt film.

thalpy of 11.4 kcal/mol, which is within the same order of magnitude for typical molecules-in-solids interaction energy.<sup>2-4</sup> It should be emphasized that  $\gamma_0$ ,  $K_0$ , and  $\theta$  are strongly dependent upon the doping process and the doping time, similar to the coverage dependence of the desorption rates of atoms and molecules from the solid surface.<sup>4</sup> Since the main objective of this paper is to discuss the laser marking process, we shall not extend ourselves further into the details of the thermal desorption measurements, which will be reported elsewhere.

The reason for thinking of a resonant laser-induced desorption experiment on the I<sub>2</sub>-doped PSt film is clearly shown in the VIS-UV absorption spectrum of the impregnated film, depicted in Fig. 3. Many of the Ar<sup>+</sup> laser lines lie within the molecular iodine absorption envelope, while the main emission of a XeCl laser (308.0 nm) coincides with the charge-transfer band. In this paper the laser marking experiments were performed using a cw Ar<sup>+</sup> laser. The diameter of the beam was controlled by drilling a 1.0- or 2.0-mm-diam hole in a metallic plate. The doped film sample was positioned behind this plate and the laser transmitted power was followed by a photodetector, with its output signal connected to a chart recorder. In Fig. 4 we show the results of a typical laser marking experiment with a 30-μm-thick PSt:I<sub>2</sub> sample doped by vapor phase during 520 h using the 514.5-nm line. This figure tells us that, exposing the PSt:I<sub>2</sub> doped film for a few seconds to the Ar<sup>+</sup> laser beam, the transmitted power at the interaction region increases with time until complete transparency is reached, leaving a clear marked spot with the laser beam shape. Furthermore, the observed time scale for reaching a marked spot is such that it decreases with increasing power, as evidenced in Fig. 4. We have attempted next to investigate the relative contribution of a photothermal versus a photodissociation process by determining the wavelength dependence of the marking time. For this set of experiments we have first substituted the laser rear

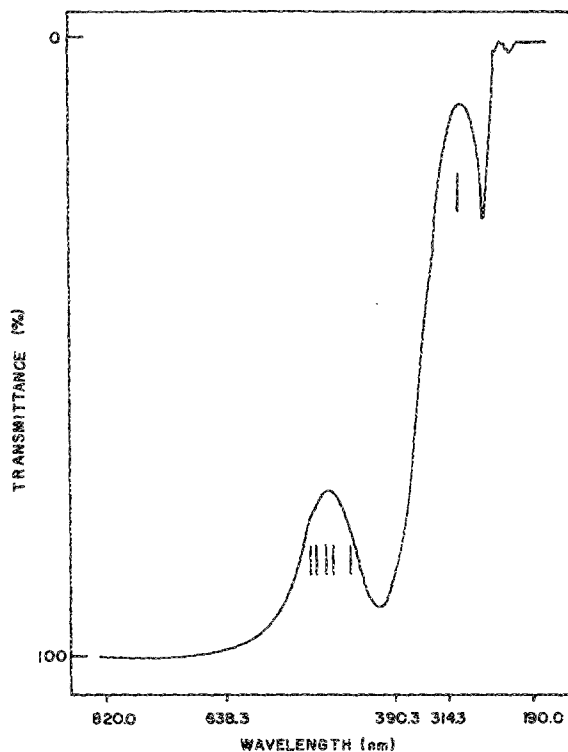


FIG. 3. Absorption spectrum of an iodine doped polystyrene film from 820 to 190 nm. In order of decreasing wavelength, the spectrum shows a molecular  $I_2$  transition at 495 nm, the PSt: $I_2$  charge-transfer band at 310 nm and PSt electronic transitions below 270 nm. Marked in the spectrum are  $Ar^+$  laser lines (around 500 nm) and the XeCl laser emission (at 308 nm).

mirror by a surface coated Littrow prism, used as a tuning element. We could, therefore, selectively choose the  $Ar^+$  laser lines at 514.5, 501.7, 496.5, 488.0, 476.5, and 457.9 nm. The laser power was fixed at 20.0 mW and transmittance measurements were performed using the 70- $\mu$ m-thick PSt films, vapor phase doped for about 520 h.

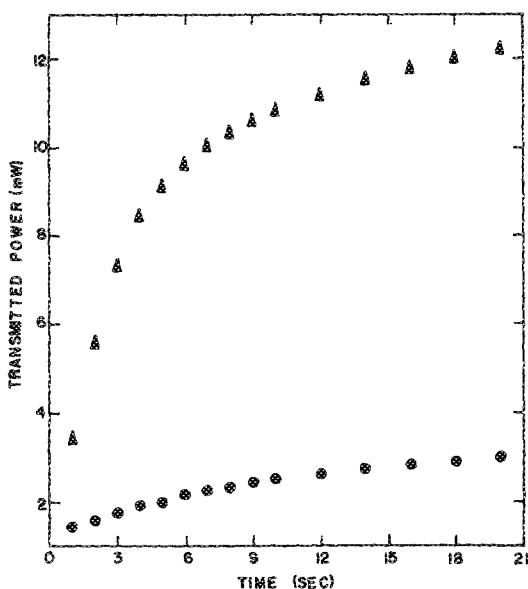


FIG. 4. The 514.5-nm  $Ar^+$  laser line transmitted power as a function of time for a 30- $\mu$ m-thick PSt film, vapor phase doped with iodine for 520 h. The circles refer to an incident power of 16 mW, whereas the triangles correspond to an incident power of 40 mW.

The observed transmitted power was computer fitted using the model developed in the next section and the parameters  $\lambda$ ,  $\sigma$ , and  $\tau$  were determined. Table I shows the values for  $\tau$ .

### III. DISCUSSION AND CONCLUSIONS

In this section we propose a simple model for explaining the main features of the cw  $Ar^+$  laser marking experiments with PSt: $I_2$  samples. Similarly to the case of pit formation by short intense laser pulses,<sup>6-8</sup> the model involves the combined effects of laser absorption and subsequent heating of the sample. Specifically, we assume that the absorbed laser power is totally or partly converted into heat due to the non-radiative deexcitation processes following the light absorption. As a result of the sample heating, the iodine concentration in the interaction region (assumed to be a cylinder of base area equal to the laser beam cross section and height equal to the sample thickness) begins to decrease due to thermally stimulated desorption. Consequently, the absorption coefficient (assumed to be proportional to the  $I_2$  concentration) also decreases which, in turn, entails in an enhancement of the transmitted laser power. The temperature rise in the sample is determined by the solution of the thermal diffusion equation. However, since our experiments were performed under cw irradiation, with exposure times much longer than the thermal diffusion time ( $t_d = l^2/\alpha$ , where  $l$  is the sample thickness and  $\alpha$  is the thermal diffusivity), we neglect the effects of the diffusion terms in the thermal diffusion equation. Denoting by  $RP_0$  the laser power loss due to reflection and scattering and by  $P_0 e^{-\gamma}$  the transmitted power where  $\gamma$  is the sample absorbance, the absorbed power may be written as  $P_{abs} = P_0(1 - R - e^{-\gamma})$ . Under these conditions, the temperature rise in the sample is governed by the equation

$$\rho c \frac{\partial T}{\partial t} = \frac{\eta P_0}{V_b} (1 - R - e^{-\gamma}), \quad (4)$$

where  $\rho$  is the sample density ( $g/cm^3$ ),  $c$  is the specific heat ( $J/g K$ ),  $V_b = lAb$  is the interaction volume, and  $\eta$  is the light into heat conversion efficiency. On the other hand, the sample absorbance  $\gamma$  in Eq. (4) decreases with increasing temperature according to Eq. (1). Thus, our claim is that by solving the coupled set of equations for  $T$  and  $\gamma$  we can calculate the time evolution of the transmitted power,  $P(t) = P_0 \exp(-\gamma)$ , and compare it with the experimental

TABLE I. The wavelength dependence of the marking time  $\tau$  and the normalized (to its value at 514.5 nm) absorption coefficient obtained from the experimental data.

line (nm)	$\tau$ (s)	$\beta$ (rel.)
514.5	9.6	1.00
501.7	7.3	1.05
496.5	8.2	1.08
488.0	6.4	1.05
476.5	6.9	0.91
457.9	3.7	0.59

data. Since this procedure is computationally quite time consuming, we shall restrict our quantitative analysis to the case of relatively small incident laser powers. Accordingly, we write  $\gamma$  as  $\gamma = \gamma_0 \Delta\gamma$ , where  $\Delta\gamma$  is the absorbance shift due to thermally induced desorption, and introduce the following notation:  $\lambda = (1 - R)$ ;  $\sigma = \exp(-\gamma_0)$ ; and  $t_c = \rho c V_b T_0 / P_0$ . Equation (4) is then rewritten as

$$\frac{\partial T}{\partial t} = \frac{T_0}{t_c} (\lambda - \sigma e^{\Delta\gamma}). \quad (5)$$

For small laser powers both the temperature rise  $T = T - T_0$  and the absorbance shift  $\Delta\gamma$  are so small that we may write them as

$$\gamma = \gamma_0 + \left( \frac{\partial \gamma}{\partial T} \right)_{T_0} \Delta T + \frac{1}{2} \left( \frac{\partial^2 \gamma}{\partial T^2} \right)_{T_0} (\Delta T)^2 + \dots \quad (6)$$

Using Eq. (1) to calculate the derivatives of  $\gamma$  with respect to  $T$  appearing in Eq. (6), and performing some straightforward calculations, one gets

$$\Delta\gamma = \gamma_0 K_0 e^{-\theta/T_0} \times \left[ \Delta T + \frac{1}{2} \left( \frac{\theta}{T_0^2} - K_0 e^{-\theta/T_0} \right) (\Delta T)^2 + \dots \right]. \quad (7)$$

Taking the derivative with respect to the time of Eq. (7) one finally arrives at the equation governing the time evolution of  $\Delta\gamma$ , namely

$$\frac{\partial \Delta\gamma}{\partial t} = \gamma_0 K_0 e^{-\theta/T_0} \times \left[ \frac{\partial \Delta T}{\partial t} + \left( \frac{\theta}{T_0^2} - K_0 e^{-\theta/T_0} \right) \Delta T \frac{\partial \Delta T}{\partial t} + \dots \right]. \quad (8)$$

Substituting into Eq. (8) the time derivative of  $\Delta T$  by Eq. (5), and keeping only the first term in the right-hand side, we find

$$\frac{\partial \Delta\gamma}{\partial t} = \frac{1}{\tau} \left( \frac{\lambda}{\sigma} - e^{\Delta\gamma} \right), \quad (9)$$

where

$$\tau = \rho c V_b / (\eta P_0 e^{-\gamma_0} \gamma_0 K_0 e^{-\theta/T_0}) \quad (10)$$

is the characteristic rising time (marking time) for the transmitted power. For small shifts in  $\gamma$ , expanding  $\exp(\Delta\gamma)$  in the right-hand side of Eq. (9) and retaining only the linear term in  $\Delta\gamma$ , one finally gets a simple linear first-order differential equation describing the time evolution of the absorbance, namely

$$\frac{\partial \Delta\gamma}{\partial t} + \frac{\Delta\gamma}{\tau} = \frac{\lambda - \sigma}{\tau \sigma}, \quad (11)$$

whose solution is

$$\Delta\gamma = [(\lambda - \sigma)/\sigma] (1 - e^{-t/\tau}). \quad (12)$$

As a check to this simple model we have used Eq. (12) in the expression for the transmitted power, namely,

$$P(t) = P_0 \sigma \exp(\Delta\gamma) \quad (13)$$

to fit the experimental data, leaving  $\lambda$ ,  $\sigma$ , and  $\tau$  as fitting parameters. In Fig. 5 we present the results we got for the normalized transmitted power ( $P/P_0$ ) for a 30- $\mu\text{m}$ -thick PSt:I<sub>2</sub> sample, doped by vapor phase during 520 h, irradiated by the 514.5-nm Ar<sup>+</sup> laser line at 16-mW power, and a laser

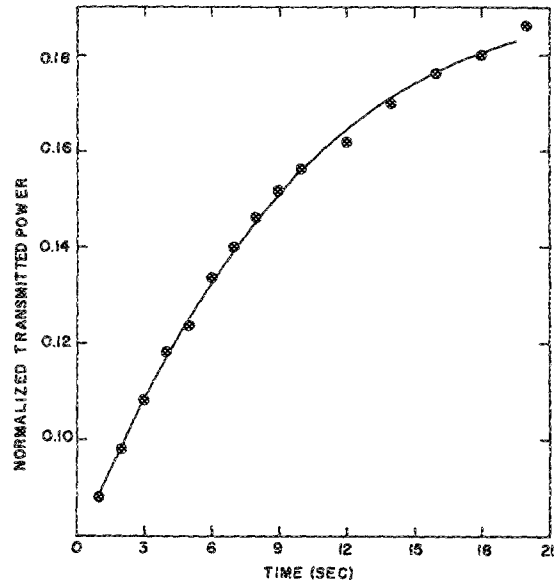


FIG. 5. The 514.5-nm Ar<sup>+</sup> laser line transmitted power as a function of time for a 30- $\mu\text{m}$ -thick PSt film, vapor phase doped for 520 h. Laser incident power was 16 mW. The solid line corresponds to the data fitting to the theoretical expressions.

beam of 1.0 mm diam. The solid curve in Fig. 5 corresponds to the data fitting using Eqs. (13) and (12) as the theoretical expression. The results we got for the fitting parameters were  $\lambda = 0.14$ ,  $\sigma = 0.077$ , and  $\tau \approx 6.14$  s. In particular, the value of  $\sigma = \exp(-\gamma_0)$ , which is essentially the transmittance at very low-power levels, agrees very well with the transmittance value of 7.5% we got in the spectrophotometer measurements at 514.5 nm. The same procedure was adopted to the different incident power levels, wavelengths, and doping methods. In Fig. 6 we show the dependence of the marking time  $\tau$  for the 30- $\mu\text{m}$ -thick PSt:I<sub>2</sub> sample, as a function of the

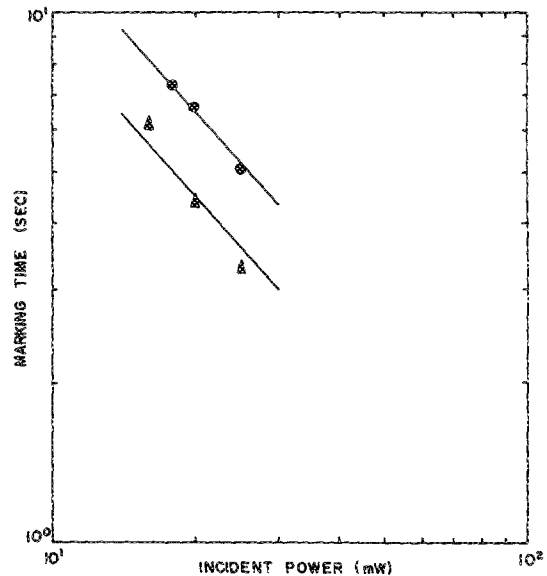


FIG. 6. Marking time vs the incident power at 514.5 nm for the solution-doped (●) and vapor-phase doped (Δ) PSt films, roughly 30  $\mu\text{m}$  thick, impregnated during 520 h.

laser power at the 514.5-nm line. Figure 6(a) corresponds to the solution doping and Fig. 6(b) to the vapor-phase doping, both impregnated during 520 h. As predicted by Eq. (10),  $\tau$  decreases with the inverse of the incident power, as suggested by the solid lines in Fig. 6 which are the results of fitting  $\tau$  as a  $P_0^{-1}$  expression. For laser powers above 30 mW, the simple analytical expression failed to fit the experimental data. This was already expected since the above expression [Eq. (10)] is valid for small laser powers such that  $\Delta T$  and  $\Delta\gamma$  are sufficiently small. For higher incident powers one should resort to the full solution of the coupled equations for  $T$  and  $\gamma$ .

Finally, let us discuss some aspects of the molecular mechanisms involved in the laser-induced heating of the iodine-doped polymer. The first coupling step between the  $\text{Ar}^+$  laser lines and the impregnated material is electronic excitation of the  $\text{I}_2 X^1\Sigma_g^+$  ground-state molecules to the  $B^3\Pi_{0+u}$  state



After that, two independent relaxation channels are possible. The electronically excited  $\text{I}_2$  molecules may transfer their energy by nonradiative processes, with a consequent local heating of the polymeric matrix. This can be represented by



where  $\text{PSt}^+$  corresponds to vibrationally excited polystyrene macromolecules and  $\Delta H$  is the generated heat. The iodine molecules would rapidly sublime because of a sudden increase in temperature.



The other possibility is that the excited  $\text{I}_2$  molecules dissociate into electronically excited and/or kinetically hot atomic species,



This has actually been observed in the gas phase for wavelengths around 500 nm.<sup>9</sup> These atoms would finally transfer their excess energy to the polymeric matrix, following steps analogous to the ones represented by Eqs. (15)–(17).

Table I summarizes the results we got for the wavelength dependence of the marking time  $\tau$ . Also presented here are the relative absorption coefficient values  $\beta$  determined for the band around 495 nm using the 70- $\mu\text{m}$ -thick film. If the main mechanism responsible for the laser marking process were the photothermal process (i.e., heating due to the optical absorption followed by nonradiative deexcitation) one would expect the marking time to vary inversely proportional to the absorption coefficient. On the other hand, if the marking process were solely governed by photodissociation, the marking time for the 514.5-nm line should be higher than that for the 457.9-nm line, since the former line is known<sup>9</sup> to have lower photodissociation quantum yield than that of the latter. The latter hypothesis is based upon the  $\text{I}_2$  photodissociation quantum yield results in the gas phase.<sup>9</sup> As shown in Ref. 9,  $\text{I}_2$  has a photodissociation

quantum yield around 1.0 for wavelengths between 500 and 470 nm, whereas for wavelengths between 500 and 525 nm, it goes down to 0.4–0.1. The results summarized in Table I tell us that the optical absorption coefficient is roughly the same between 514.5 and 476.5 nm, and exhibits a sharp decrease for the 457.9-nm line. As for the values of  $\tau$ , Table I tells us that  $\tau$  is largest for the 514.5-nm line ( $\sim 9.6$  s), and remains roughly constant around 7.2 s, between 501.7 and 476.5 nm, and decreases sharply to 3.7 s for the 457.9-nm line. According to the photothermal mechanism, one would expect a roughly constant marking time in the region of constant absorption coefficient, namely, between 501.7 and 476.5 nm, as observed in Table I, and a longer marking time for the 457.9-nm line which has a smaller absorption coefficient. In contrast, for the 457.9-nm line,  $\tau$  exhibits a sharp decrease. This sharp decrease in  $\tau$  at the 457.9-nm line seems to indicate that, at least for this line, the photodissociation mechanism is probably dominating the marking process. Furthermore, a second evidence in favor of the photodissociation mechanism comes from the experiment with the 514.5-nm line. The longer marking time for this line, as compared with those having the same absorption coefficient (namely, the lines between 501.7 and 476.5 nm) as well as with 457.9-nm line, may only be attributed to the contribution of the photodissociation mechanism. In Fig. 7 we show the dependence of  $\tau$ , normalized to its value at 514.5 nm as a function of the wavelength. This is represented by the circles in Fig. 7. Also shown by the solid lines in this figure are the expected behavior of the marking times if pure photothermal and photodis-

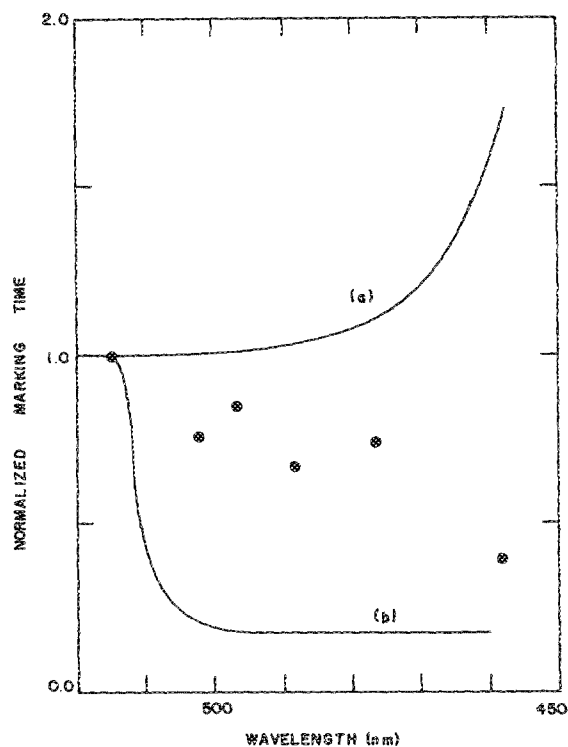


FIG. 7. Normalized marking time, to its value at 514.5 nm, as a function of the wavelength. The circles correspond to the data shown in Table I. The solid lines correspond to the expected behavior of the normalized marking times if (a) pure photothermal and (b) photodissociation processes were taking place separately.

sociation processes were taking place separately. These times, normalized to the corresponding values at 514.5 nm, are inversely proportional to the absorption coefficient and photodissociation quantum yield, respectively. The curve for the normalized photodissociation marking time was obtained using the data for the photodissociation quantum yield  $\phi$  of Ref. 9 [i.e.,  $\phi(514.5)/\phi(\lambda)$ ], whereas the photothermal marking time was obtained using the data for  $\beta$  given in Table I. Figure 7 shows that there is indeed a competition between these two mechanisms with a tendency for photodissociation to dominate the marking process.

#### IV. CONCLUSIONS

In conclusion, we have discussed in this paper the possible mechanisms responsible for the laser marking capability of PSt:I<sub>2</sub>-doped films. The laser marking experiments were performed using an Ar<sup>+</sup> laser whose lines lie within the I<sub>2</sub> absorption envelope. Experiments with high-power (25 mW) He-Ne laser showed no marking capability, which means that we are dealing with a resonant laser-induced process. The two mechanisms considered for explaining the marking process were the photothermal and the photodissociation localized heating. The evidences summarized in Table I seem to indicate that the photodissociation is the domi-

nant mechanism. The apparent high effectiveness of the photodissociation process is probably related to the following facts: (i) It is a very fast ( $\sim 10^{-12}$  s) and efficient process, especially for  $\lambda < 500$ -nm excitation of I<sub>2</sub>; and (ii) The generated kinetically hot I atoms seem very effective in transferring their excess energy to the polymer lattice vibrations, thereby producing a localized increase of temperature with a consequent increase in the I<sub>2</sub> desorption rate.

#### ACKNOWLEDGMENT

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