Photoacoustic investigation of iodine-doped polystyrene

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The kinetics of iodine doping of atactic polystyrene films is investigated using photoacoustic spectroscopy. The changes in the photoacoustically measured physical properties, such as nonradiative relaxation time and thermal diffusivity, are present as a function of the doping time. The results show strong evidence that an order-disorder transition is taking place as a function of the doping time. The suggested order-disorder transition is also evident in the dielectric constant measurements of the doped films.

I. INTRODUCTION

Polystyrene (PST) is a well-known insulating material which can have its electrical properties easily changed by chemical¹ and physical² methods. The ease of changing the electrical properties of PST is due to the fact that PST has delocalized aromatic π electrons which act as charge donors.³ In a previous study,⁴ the capability of iodine (I_2)-doped PST films for laser marking has been demonstrated. The marking capability of these PST: I_2 films was evidenced as follows: Exposing, for a few seconds, the PST: I_2 -doped films to a cw Ar⁺ laser, the interaction region changes its color from red to transparent, leaving a clear marked spot with the laser beam shape. This marking process is erasable, i.e., the film can regain its original color by exposing it again to I_2 vapor.

In this study we report on the use of photoacoustic spectroscopy (PAS) to investigate the kinetics of the iodine-doping process. The versatility as well as the potentiality of PAS as a material characterization technique has been reviewed by several authors.⁵⁻⁷ Apart from providing direct optical absorption spectra, the PA technique can also be used to perform depth profile analysis, characterization of thermal properties,⁸⁻¹⁰ as well as investigation of nonradiative relaxation processes.¹¹⁻¹⁴ In a typical PA experimental arrangement a sample enclosed in an airtight cell is exposed to a chopped light beam. The resulting periodic heating of the sample is strongly dependent upon the interplay of three factors, namely, optical absorption coefficient at the incident radiation wavelength, light-into-heat conversion efficiency, as well as heat diffusion through the sample. Dependence of the PA signal on the optical absorption coefficient allows us to perform spectroscopy, whereas the fact that the signal is also dependent upon the light-into-heat conversion efficiency means that the detected signal is sensitive to the non-radiative deexcitation processes within the sample. Finally, the fact that the PA signal depends on how the heat diffuses through the sample allows us to perform not only thermal characterization of the sample (i.e., measurements of its thermal properties) but also to conduct thermal imaging.

II. EXPERIMENT

The iodine doping of polystyrene was investigated using especially prepared atactic PST films. The PST resin used was manufactured by Estireno do Nordeste S. A. and was free from additives. The films were cast from a chloroform solution at room temperature over a flat clean glass substrate. A 5% (w/w) solution was found optimum for producing homogeneous, pinhole-free, transparent films. The iodine doping was accomplished by exposure of the PST films to vapor phase iodine.

The photoacoustic spectra were recorded using a 1000-W xenon lamp, whose polychromatic beam was modulated using a variable speed chopper (PAR Model 192) and later focused onto a Jobin-Yvon monochromator. The output monochromatic beam was then focused onto the sample placed inside an EDT photoacoustic cell with a built-in BK capacitive microphone. The microphone signal was then recorded as a function of the incident monochromatic light wavelength, using a lock-in amplifier (PAR Model 124). The spectral bandwidth used was kept at 10 nm. The photoacoustic thermal diffusivity measurements were carried out using the open photoacoustic cell (OPC) technique, as described in Refs. 15 and 16. This technique consists of mounting the sample directly onto a cylindrical electret microphone. The typical design of an electret microphone consists of a metallized electret diaphragm (12- μ m Teflon with a 500-1000-Å-thick deposited metal electrode) and a metal backplate separated from the diaphragm by an air gap (45 μ m). The metal layer and the backplate are connected through a resistor R . The front sound inlet is a circular hole of 2 mm diam and the front air chamber adjacent to the metallized face of the diaphragm is roughly 1 mm long. As a result of the periodic heating of the sample by the absorption of modulated light, the pressure in the front chamber oscillates at the chopping frequencies, causing diaphragm deflections, which generates a voltage across the resistor R . In other words, the proposed technique consists of using the front chamber of the microphone itself as the usual gas chamber of conventional photoacoustics. The heating of the

FIG. 1. Photoacoustic spectrum of a 26- μm -thick PST:I₂ film recorded at 42 Hz.

sample was accomplished using a 500-W halogen lamp whose modulated polychromatic beam is directly focused onto the sample.

III. PA SPECTROSCOPY

In Fig. 1 we show a typical PA spectrum of a 26- μm -thick PST:I₂-doped film recorded at 42 Hz. The spectrum shown in Fig. 1 corresponds to a 300-min doping time. As compared to undoped PST, which exhibits strong absorption bands below 270 nm, two new bands are present in the PA spectrum of PST:I₂-doped samples; One between 420 and 580 nm with maximum absorption around 495 nm, and a stronger one, between 270 and 420 nm, with peak absorption centered at 310 nm. These two bands are characteristic of the charge-transfer complex formation.^{4,17} The 495-nm band is due to the I₂ molecular band which, in solutions with noninteracting solvents (like, CCl₄), is located at 520 nm (Ref. 18) but tends towards the blue with increasing donor concentration. The second, stronger band at 310 nm, is assigned to PST-to-I₂ charge transfer, similarly to those observed in other systems.^{17,19} The 495-nm band is responsible for the deep red color as well as for the Ar⁺ laser marking capability⁴ of the doped PST films.

FIG. 2. Modulation frequency dependence of the 310-nm band for a 26- μm -thick PST:I₂ film. The I₂ doping time was 180 min, and the solid line corresponds to a power law data fitting showing that the signal amplitude varies as $f^{-1.4}$.

In Fig. 2 we show the modulation frequency dependence of the 310-nm band for a 26- μm -thick PST:I₂ film doped for 180 min. The signal exhibits a $f^{-1.4}$ modulation frequency dependence which is in very close agreement with the $f^{-1.5}$ predicted for a thermally thick sample by the thermal diffusion model of Rosencwaig and Gersho²⁰ for the generation of the PA signal. In fact, using the Rosencwaig-Gersho theory, modified to include the effect of a finite nonradiative deexcitation time, the pressure fluctuation in the PA cell is given by^{14,20}

$$\delta p = \frac{\gamma P_0 I_0 \beta}{2\sqrt{2} l_g T_0 k_s a_g (\beta^2 - \sigma_s^2) (1 + j\omega\tau)} \left(\frac{(r-1)(b+1)e^{l_s\sigma_s} + (r+1)(1-b)e^{-l_s\sigma_s} - 2(r-b)e^{-\beta l_s}}{(1+g)(1+b)e^{l_s\sigma_s} - (1-g)(1-b)e^{-l_s\sigma_s}} \right) e^{j\omega t - (\pi/4)} \quad (1)$$

where γ is the air specific heat ratio, $P_0(T_0)$ is the ambient pressure (temperature), I_0 is the incident light intensity at a given wavelength, l_i , k_i , and $\alpha_i = k_i/\rho_i c_i$ are the length, thermal conductivity, and thermal diffusivity of material i , respectively, and β and τ are the sample optical absorption coefficient and the nonradiative relaxation time at the illumination wavelength. Here, the subscript i denotes the samples (s), gas (g), and backing (b) media, respectively, $\sigma_i = (1+j)\alpha_i$, with $\alpha_i = (\pi f/\alpha_i)^{1/2}$ is the complex thermal diffusion coefficient of material i , and $g = k_g a_g/k_s a_s$, $b = k_b a_b/k_s a_s$, and $r = \beta/\sigma_s$. For a thermally thick sample, the thermal diffusion length, α_s^{-1} , is much smaller than the

sample thickness, namely, $l_s \sigma_s \ll 1$; Eq. (1) reduces to

$$\delta p = \frac{\gamma P_0 I_0 \beta \alpha_s^{1/2}}{4\pi\sqrt{2} l_g T_0 k_s f^{3/2} (1+g)} \frac{e^{j\omega t - (\pi/4)}}{[1 - (\beta/\sigma_s)] (1 + j\omega\tau)} \quad (2)$$

Equation (2) means that the PA signal is proportional to the optical absorption coefficient provided $\beta/\sigma_s < 1$, and that it varies as $f^{-3/2}$ for $\omega\tau \ll 1$. The latter condition is usually well satisfied whereas the first condition requires that the thermal diffusion length $(\alpha_s/\pi f)^{1/2}$, be much smaller than the optical penetration depth, β^{-1} . For lightly doped (i.e., transparent) samples it is again well satisfied for atactic PST films in

the modulation frequency range of our experiments.

The modulation frequency dependence of the phase of the PA signal in the thermally thick regime of our experiments is obtained from Eq. (2) by rewriting it as $\delta p = |\delta p| \exp[j(\omega t + \phi)]$. One gets

$$\phi = -(3\pi/4) - \tan^{-1}(\omega\tau) + \tan^{-1}\left[1/(\sqrt{2\omega\tau_\beta} + 1)\right], \quad (3)$$

where $\tau_\beta = 1/\beta^2\alpha_s$. The above equation indicates that the phase change of the PA signal with the modulation frequency of a given absorption band depends not only on its nonradiative relaxation time, τ , but also on the thermal diffusion time within the optical penetration depth. As mentioned in Sec. I, this modulation frequency dependence of the PA signal phase has been used by several authors¹¹⁻¹⁴ to study the behavior of τ in collisional deactivation of vibrational excitation in gases and in radiationless relaxation of dopant ions in crystals and glasses. We have carried out the fitting of the PA signal phase data of the 310- and 495-nm bands to extract information on how the kinetics of I_2 doping affects τ and τ_β . In Figs. 3 and 4 we show the dependence on the doping time of τ and τ_β of these two bands, respectively, whereas in Fig. 5 we show a typical result of the PA signal phase data fitting. Figure 5 refers to the PA phase data for a 5-h-doped sample at the 495-nm band.

Figures 3 and 4 show that τ exhibits a minimum between a doping time of 120–180 min, whereas τ_β exhibits a minimum around 120 min. The behavior of τ_β is essentially determined by the dependence of the thermal diffusivity α_s (i.e., $\tau_\beta = 1/\beta^2\alpha_s$) on the doping time. In fact, the measurements of the thermal diffusivity, reported in the next section, show that the thermal diffusivity exhibits a peak at exactly the same point where τ_β exhibits a minimum. To explain this

FIG. 3. Dependence of the nonradiative relaxation time on the iodine doping time for the (a) 310-nm and (b) 495-nm absorption bands, as obtained from the PA phase data fitting.

FIG. 4. Dependence of the characteristic time τ_β on the iodine doping time for the (a) 310-nm and (b) 495-nm absorption bands, as obtained from the PA phase data fitting.

behavior we first note that the photoacoustically measured relaxation time, τ , is not necessarily that appropriate to the level initially excited in the absorption process but rather it is the average lifetime of the energy contained in a variety of states before becoming heat. Thus, in general, we can have a nonunique relaxation pathway consisting of several successive steps, and the measured lifetime is an average lifetime for heat production. Physically, the presence of a minimum in τ as well as the sudden change in τ_β (or α_s) may be attributed to the onset of a second-order phase transition.²¹ In a second-order phase transition, contrary to the case of a first-order transition, there is no latent heat. The presence of a latent heat suggests that the sample may be viewed as a heat sink at the transition point; i.e., we have to wait quite some

FIG. 5. Photoacoustic phase angle at the 495-nm band as a function of the modulation frequency for a 5-h doped polystyrene sample. The solid line corresponds to the fitting of the experimental data to the theoretical expression.

time for the heat to diffuse through the sample at the transition point. Thus, at a transition point, we should expect the PA signal to exhibit a decrease since less heat is reaching the gas of the PA chamber. We therefore expect τ to experience a rise at a first-order phase transition. In contrast, at a second-order phase transition the derivative of the thermodynamic functions (i.e., specific heat, thermal expansion, thermal conductivity, etc.) is discontinuous at the transition point. In particular, both α_s and k_s exhibit peaks at the transition point so that the average lifetime for heat production, τ , is expected to decrease as we cross over a second-order phase transition.

IV. THERMAL DIFFUSIVITY

The thermal diffusivity measurements were carried out using the OPC technique as mentioned above. For OPC configuration, schematically shown in Fig. 6, the pressure fluctuation in the air chamber is given^{15,16} by

$$\delta p = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi l_g T_0 k_s f \sinh(l_s \alpha_s)} e^{[i\omega t - (\pi/2)]} \quad (4)$$

In arriving at Eq. (4) we have assumed that the sample is optically opaque and that the heat flux into the surrounding air is negligible. The implicit optical opaqueness condition, meaning that all the incident radiation is fully absorbed at the surface $z = -l_s/2$ (cf. Fig. 6), was ensured by using a thin circular Al foil (20 μm thick) of 8 mm diam, attached to the front side of the sample using a thin layer of vacuum grease. The Al foil was coated with a thin layer of black ink to enhance the light absorption. The thermal diffusion time $\pi l^2/\alpha$ in this Al foil is of the order of 13.6 μs [$\alpha(\text{Al}) = 0.92 \text{ cm}^2/\text{s}$] so that the heat generated in the Al foil absorber may be assumed to be instantaneously transmitted to the PST samples. For a thermally thin sample (i.e., $l_s \alpha_s \ll 1$), Eq. (4) reduces to

$$\delta p \approx \frac{\gamma P_0 I_0 \alpha_g^{1/2} \alpha_s}{(2\pi)^{3/2} T_0 l_g l_s k_s} \frac{e^{[i\omega t - (3\pi/4)]}}{f^{3/2}} \quad (5)$$

In other words, the PA signal amplitude decreases as $f^{-1.5}$ as one increases the modulation frequency. In contrast, at high modulation frequencies, such that the sample is thermally thick (i.e., $l_s \alpha_s \gg 1$), one gets

$$\delta p \approx \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{\pi T_0 l_g k_s} \frac{\exp[-l_s (\pi f / \alpha_s)^{1/2}]}{f} \times e^{[i\omega t - (\pi/2) - l_s \alpha_s]} \quad (6)$$

FIG. 6. Open-cell geometry used in the calculations.

Equation (6) means that, for a thermally thick sample, the amplitude of the PA signal decreases exponentially with the modulation frequency as $(1/f)\exp(-a\sqrt{f})$, where $a = (\pi l_s^2 / \alpha_s)^{1/2}$. The thermal diffusivity α_s can then be obtained from the signal data fitting in the high modulation frequency range from the coefficient $a = (\pi l_s^2 / \alpha_s)^{1/2}$ expression

$$S = (A/f)\exp(-a\sqrt{f}). \quad (7)$$

The PA thermal diffusivity measurements were carried out using a 500-W halogen lamp whose polychromatic beam was modulated using a variable speed chopper (PAR Model 192) and later focused onto the sample. The microphone voltage output was measured using a lock-in amplifier (PAR Model 124). In Fig. 7 we show the PA signal amplitude as a function of the modulation frequency square root for a 30- μm -thick, 8-mm-diam PST:I₂-doped sample, after 2 h of I₂ vapor exposure. The solid curve in this figure represents the fitting of the experimental data to Eq. (7). The resulting value obtained for α from the data fitting was $\alpha = 0.00136 \text{ cm}^2/\text{s}$ for the 2-h PST:I₂-doped sample. For the undoped PST sample, the value we got for α was $0.00084 \text{ cm}^2/\text{s}$, which agrees very well with the known value (i.e., $\alpha = 0.00086 \text{ cm}^2/\text{s}$) of the thermal diffusivity for the atactic PST. The same procedure was repeated with all the other PST:I₂-doped samples. In Fig. 8 we summarize the results for the thermal diffusivity of our PST:I₂-doped samples as a function of the doping time. We note that, at a 120-min doping time, α exhibits a sudden change, reaching a peak value of $0.00136 \text{ cm}^2/\text{s}$ and then decreases on further increasing the doping time up to 150 min, where it reaches a minimum of the order of $0.00094 \text{ cm}^2/\text{s}$. On further increasing the I₂ exposure time for 150 min, α increases, reaches another maximum around 180 min and then decreases with increasing doping time. The overall behavior of α versus the doping time showed in Fig. 8 is the inverse of that observed in Fig. 4 for τ_β . The tentative explanation that the sudden change around 120 min is related to an order-disorder transition is also supported by the results of Fig. 8. Above 200 min α decreases with increasing doping time. This behavior would be expected if both the mass density and the specific heat increased with increasing doping time; note that $\alpha = k/\rho c$, where c is the specific heat. The mass incorporation into our sample was monitored as a function of the I₂-doping time. This is shown in Fig. 9 in which a 23% increase in the mass of

FIG. 7. PA signal amplitude, as a function of the square root of the modulation frequency, for a 30- μm -thick PST:I₂-doped sample after 2 h of I₂ doping. The solid line corresponds to the fitting of the experimental data to the theoretical expression.

FIG. 8. Thermal diffusivity of PST:I₂-doped samples as a function of the doping time.

a 20- μ m-thick PST sample is observed after 5 h of I₂ impregnation. On the other hand, between 200- and 300-min I₂ doping, the thermal diffusivity data (cf. Fig. 8) indicate that it has decreased roughly 54%. Thus, the mass variation (increase in ρ) due to the I₂ doping cannot alone account for the observed decrease in α . We then conclude that the specific heat should also increase in this region. This later hypothesis is consistent with a second-order phase transition idea. As is well known,²¹ in a second-order phase transition the specific heat is greater in the ordered state than in the disordered state.

As a final check on this hypothesis of an order-disorder transition taking place around 120 min of I₂ doping, we have carried out the dielectric constant measurements of our doped samples. The capacitance measurements were carried out using a Hewlett-Packard Model 4274A LCR meter in the frequency range between 100 Hz and 100 kHz.² The disklike samples with a diameter of 1 cm and thicknesses between 24 and 29 μ m were previously exposed to I₂ vapor at different time intervals. In Fig. 10 we show the dependence of the dielectric constant, ϵ/ϵ_0 , measured at 1 kHz, as a function of the sample doping time. Figure 10 shows that the dielectric constant remains practically constant around the value of 2.52 for the pure PST up to 2 h of I₂ doping. At 120 min of I₂ doping the dielectric constant suffers a sharp decrease towards the value of 2.05 and remains practically constant at this value for longer doping times. The same general behavior of ϵ/ϵ_0 was also observed at all the frequencies used in our measurements. The solid curve in Fig. 10 is the result of the corresponding data fitted to a theoretical expression describing the sudden jump. The trial function we have used

FIG. 9. Mass change of a 20- μ m-thick PST film as a function of the I₂-doping time. The solid line is the linear regression fitting to the data.

FIG. 10. Dielectric constant of the PST:I₂-doped samples, at 1 kHz, as a function of the I₂-doping time. The solid line corresponds to the results of the data fitting to the theoretical expression describing a "knee".

was an exponential-like function to describe the knee around 120 min. Mathematically, a knee may be described by a function of the form

$$f(t) = A / [1 + e^{(t - t_0)/\tau}], \quad (8)$$

where A is the knee height, t_0 describes the knee location, and τ represents its halfwidth. For the 1-kHz data shown in Fig. 10, the resulting expression we got was

$$\epsilon/\epsilon_0 = 2.065 + [0.472 / (1 + e^{(t - 122.31)/7.22})], \quad (9)$$

which means that the sharp transition observed in Fig. 10 is centered at 122.31 min. For all the other frequencies used in our measurements, the data fitting yielded practically the same values for the parameters t_0 and τ describing the knee, except for small changes in both the value of the independent term in Eq. (9) (it varied from 21.7 at 100 Hz to 2.05 at 10 kHz) and that of the knee height (it varied from 0.402 at 100 Hz to 0.486 at 10 kHz). In general, a discontinuity in the dielectric constant is associated with some sort of order-disorder transition.²¹ Thus, from a qualitative point of view, the sudden drop in the dielectric constant observed in Fig. 10 around 122 min may then be thought to mark the transition to an *ordered* state in which the directions of the dipoles form a regular array. The smaller value of the dielectric constant in this somewhat *ordered* state means that to cause the same change in the polarization of the system one requires a stronger electric field than in the case of the disordered state; i.e., in an ordered state it is more difficult to cause a reorientation of the dipoles than in a disordered state. We believe the above interpretation accounts reasonably, at least qualitatively, for the behavior of our data. Nevertheless, we should mention another effect that could be related to our observations, namely, the formation of I₂ clusters. However, the difficulty here is that, if I₂ clusters were being formed, we would expect that the dielectric constant would exhibit a continuous change as a function of the doping time and not an abrupt one, as shown in Fig. 10. Furthermore, the change in the value of ϵ would be towards a larger value (solid iodine has a dielectric constant of roughly four) instead of a smaller one, as in the case of our measurements. These points seem to favor the phase transition model for a qualitative description of our measurements. The observation that the dielectric constant remained at a value close to the pure PST constant is a strong indication that the transition is related to a structural change of the macromolecule.

V. CONCLUSIONS

In this study we have described a simple method for I_2 doping of atactic PST films involving the direct exposure of the polymer film to I_2 vapor. Although relatively slow, the method proved to lead to reasonable dopant stabilization. The kinetics of the I_2 doping was followed using photoacoustic spectroscopy. The PA spectra of the doped PST exhibited the characteristic I_2 molecular band around 495 nm and the PST: I_2 charge-transfer band at 310 nm. The evolution of the PA relaxation times, τ and τ_B , at these two bands as a function of the doping time was monitored in a wide doping time interval. A sudden change in τ , τ_B , α , and ϵ was observed after roughly 2 h of I_2 doping. At least qualitatively, this effect was attributed to the onset of some sort of order-disorder transition of the I_2 -doping process. In the supposedly ordered phase the directions of the dipole form a regular array.

Actually, the suggested onset of an order-disorder transition in the PST: I_2 samples seems to be in good agreement with the known structural changes that take place in the case of conducting polymers. It is generally accepted as a good model for explaining the properties of doped polymeric systems that their structure should be similar to that of the well-known organic metal-type crystals, like the Bechgaard salts.²² In this case of radical cation salts, the organic part of the crystalline structure is arranged in stacks, in general consisting of one or more condensed aromatic rings laid on top of other similar molecules. In a similar way, the dopant species also arrange themselves in a stack configuration, forming a parallel array to the organic part. Thus, the final structure consists of a sort of *interpenetrating* crystals, with two physically independent arrangements.²³ The main responsible for the electrical conductivity in such systems is the interaction between the π -type orbitals of neighboring organic rings in the stack direction. An anisotropy is expected, and actually observed, in the electrical behavior of these systems.

FIG. 11. Schematic illustration of the packing in conduction polymers. The polymer segments are represented by the circle and the dopants by the squares. The stack arrangement is in the direction normal to the paper.

Along the stack direction the electrical conductivity is 10^2 – 10^3 times higher than along the normal to the stack direction.²³ The interaction between the aromatic rings of different stacks is intermediated by the dopant species. By analogy to these Bechgaard salts, it is accepted that the main conduction path in doped polymer materials is the delocalized π electrons on the main polymer chains and that the dopant ions or molecules are responsible for the interchain interaction. The final structure in the doped polymer systems is then similar to the organic metal-type crystals, consisting of two independent arrangements of polymer segments and dopants. Although the polymer molecules do not arrange themselves in an identical way as a typical crystal (they generally show partial crystallinity), higher conductivity seems to be related to well-organized segments, and actually observed in various conducting polymers.²⁴ This is illustrated schematically in Fig. 11.

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