

Photo-electret studies of pure and doped polystyrene films

I. M. Talwar

Department of Physics, Kurukshetra University College, Kurukshetra-132119, India

and A. P. Srivastava and H. C. Sinha*

Solid State Physics Laboratories, University of Saugar, Saugar-470 003, India

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The photoelectret properties of pure and acrylic acid (AA) doped polystyrene (PS) films formed by an isothermal immersion technique have been studied. The photoelectrets were formed by simultaneous application of u.v. radiation for a short time period (2–10 min) and d.c. electric field (3–18 V). The depolarization current was obtained by reilluminating the photoelectret with the same radiation. It is found that the photo depolarization current increases with polarizing voltage and is greater for the doped samples than for the undoped samples, prepared under identical conditions. The current increases with the dopant concentration and with duration of polarization. The total charge, found by integrating the depolarization current–time curve of doped photoelectrets, tends to saturation at a certain voltage value. Doped PS gives better photoelectrets.

(Keywords: photoelectret; isothermal immersion technique; depolarization current; doped samples; saturation)

INTRODUCTION

The photoelectret effect in single crystals of sulphur was first noted by Nadzhakov¹ in 1937. Since then, there have been a number of studies on photoconduction in polymers^{2,3}. Pillai and Ahuja⁴ have reported that the photo response of polymers can be considerably improved by doping. Shrivastava *et al.*⁵ have shown that the photoelectrets of the doped polymer have longer life than those prepared from pure polymers. In the present investigation persistent internal polarization (photoelectret) studies of pure polystyrene (PS) films and those doped with acrylic acid (AA) have been reported.

EXPERIMENTAL

Cylindrical films of PS (commercial) (thickness $\sim 30 \mu\text{m}$) were prepared by an isothermal immersion method with a specially designed assembly described previously⁶. The preliminary studies were carried out on the undoped samples only. Photoelectrets were prepared by simultaneous application of the electric field (8 kVcm^{-1}) and u.v. radiation (mercury lamp) for 5 min. One of the electrodes was in the form of a mesh, and the other was the substrate. Although the properties of cylindrical films are essentially the same as those of flat films⁷ the studies of electrets in a cylindrical configuration are more useful because of their possible use in bioengineering⁸ and as prosthetic agents⁹. The photoelectrets were preserved in the dark for 30 s and were then depolarized with or without the same radiation. The current released was measured by feeding the output from the sample to a Keithley electrometer (model 610 C), coupled to an X–Y/t

recorder. A fresh sample was made for each run. The following modes of polarization and depolarization were studied.

Samples polarized in the dark, depolarized in the dark (dark–dark); polarized in photo, depolarized in dark (photo–dark); polarized for the first half in photo and for the second half in dark and depolarized in photo (photo/dark–photo); polarized in photo, depolarized in photo (photo–photo). As is evident from *Figure 1*, similar behaviour of all the curves is displayed. An initial faster decay followed by a slower one shows that there are shallow traps present (due to the localized energy states present in the amorphous commercial PS) and deep traps (due to the presence of phenyl group in PS). This is in agreement with the observations of others^{10,11a}. Furthermore, the photo–photo curve lies at the top and the dark–dark curve at the bottom, indicating the role of u.v. photons in releasing more charge carriers. So, further studies on the doped samples were carried out on this polarization/depolarization mode.

To compare the results of the doped and undoped samples, the concentration of AA was varied from 3 to 30% (by weight). The results for low concentration (5%) and the optimum concentration (25%) only are presented here, along with those on undoped samples. The optimum concentration was determined by the TSD studies, as shown earlier¹². Furthermore, to see the effect of polarizing field and polarizing time on the characteristics of PS and PS–AA photoelectrets the polarizing voltage was varied from 3 to 18 V (polarizing field 1 to 8 kVcm^{-1}) and polarizing time from 1 to 8 min.

RESULTS

The total charge, released to the external circuit, was

* Present address: Department of Physics, Government Science College, Durg, M.P. 491002, India

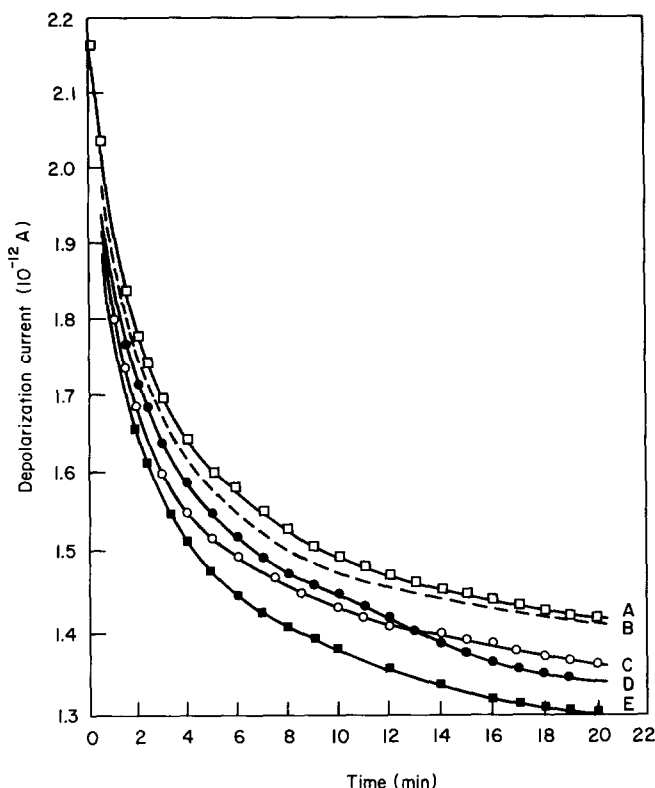


Figure 1 Depolarization current versus time curves for undoped PS. Polarizing voltage 12 V, time of polarization field 5 min, under different modes of polarization. (A) Photo-photo, (B) dark-photo, (C) photo/dark-photo, (D) photo-dark, (E) dark-dark

calculated by integrating the curve over time, $Q = \int I \cdot dt$, for the doped and undoped samples. This charge, as a function of polarizing voltage, is plotted in Figure 2. It is clear from Figure 2 that the charge is greater for the doped samples than for the undoped samples. The charge increases with the field for the undoped and low concentration doped samples without any saturation, but for the optimum concentration there is a saturation at 9 V (3 kVcm^{-1}).

The effect of polarizing time is shown by typical curves reproduced in Figure 3. It is observed that both the initial and final currents (current after 20 min) increase with exposure time. Moreover, the current and hence the charge (proportional to initial current/10) are more for the doped samples than for the undoped samples.

DISCUSSION

A photoelectret is formed by the simultaneous application of a polarizing voltage and radiation. Under exposure to radiation the photons cause the excitation of electrons from the valence band to the conduction band, where they move in the direction of the applied field until they are trapped at the structural level¹³. Re-irradiation of the sample produces charges that move under the influence of the internal field in such a way as to neutralize the polarization and give rise to a depolarization current that flows in a direction opposite to that of the polarization. As time elapses the current gradually decays implying a decrease in the number of free charge carriers. At this time the carriers trapped well inside the forbidden gap (deep traps) start contributing to the depolarization current, accounting for the initially fast and subsequently slower decay. Thus, the formation of photoelectrets in polymers

can be explained on the basis of an energy band model, according to Pohl *et al.*¹⁴ polymers are electronic conductors and the usual band theory can be applied to describe their conducting properties. McCubbin¹⁵ has attributed bands in polymers to individual macromolecules, having insignificant interchain interaction ('standard semiconductor model'¹⁶). The structure of a polymer is far from perfect as macromolecules have difficulty in aligning themselves in an ordered array¹⁷⁻²⁰. Even crystalline polymers are somewhat semi-crystalline consisting of lamellae of folded (or sometimes extended) chains, inter-linked by molecules and alternating with disordered phase regions¹³.

The photogeneration process may be viewed as a two-step process²¹. In the first step, the absorbed photon excites the electron from its ground state to some excited bound state. From the excited state, the electron may undergo thermalization/autoionization into a continuum state. Once the electron or hole reaches the continuum state it can be treated classically. It is assumed that the end product of thermalization/autoionization process is a distribution of electron-hole/pairs $g(r, \theta)$, where r is the separation between the electron and the hole, and θ is the angle their separation vector makes with the applied field. The field electrons and holes are now considered to drift

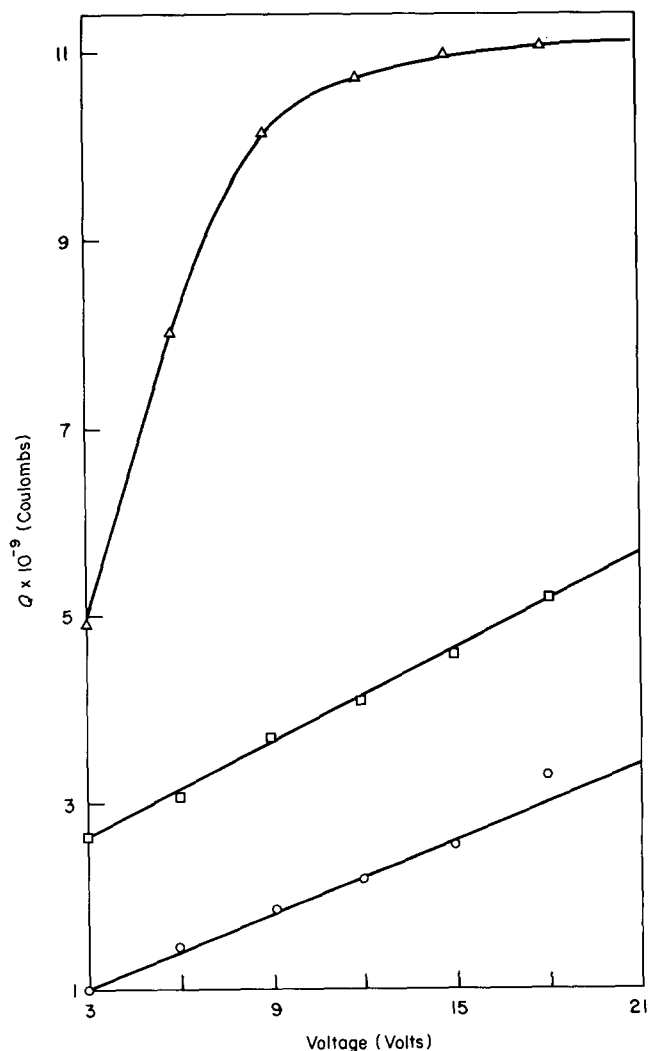


Figure 2 Total charge versus polarizing voltage. Polarizing time, 5 min. (O-O) undoped; (□-□) low concentration; (Δ-Δ) optimum doped concentration

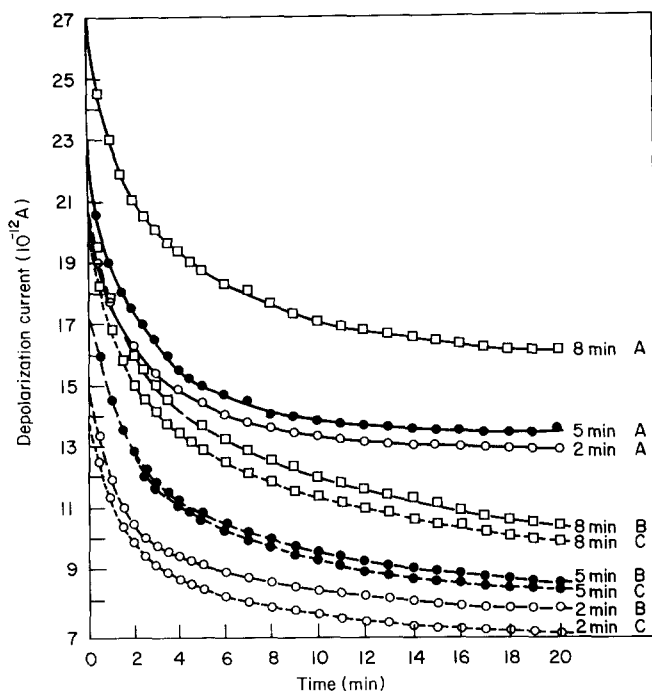


Figure 3 Depolarization current versus time for different polarization times (2, 5, 8 min) for undoped and doped samples. Curves A, B, C are for optimum concentration, low concentration and undoped samples, respectively, polarizing voltage = 15 V

under the influence of their mutual coulomb attraction and the applied field. This gives rise to the field-dependent photogeneration efficiency.

$$\phi(E) = \phi_0 \int_0^{\infty} f(r, \theta, E) g(r, \theta) d^3r \quad (1)$$

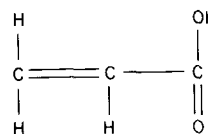
where ϕ_0 is the yield of electrons into continuum states per absorbed photon and $f(r, \theta, E)$ is the probability that the separation between the electron and hole will become large.

The measurement of photodepolarization current in doped and undoped samples under the conditions mentioned above, and in view of the state of affairs of formation of a photoelectret in polymers, we are in a position to discuss this phenomenon in PS. As is evident from *Figure 2* the charge released to the external circuit increases with the applied field. Since PS is a non-polar polymer, dipoles cannot be the main cause of polarization. The presence of heavy side phenyl groups and the atactic arrangement of substituents on successive carbon atoms make commercial PS almost amorphous. But there is evidence that there is a basic structural unit in the amorphous polymers²². Cherskasov *et al.*²³ have indicated that the photoelectret formation in PS is due to the dissociation of excitons, generated by optical excitation, into free electrons. The electrons move comparatively freely in the direction of the applied field over the microscopic distances before they fall into traps from where they can be released only on receiving the appropriate energy. The structural unit and the phenyl group, present in PS, provide shallow and deep traps respectively¹², for the charge carriers produced during the photo-electret formation. On re-irradiating the photo-electret these charges are released as the depolarization current. More and more charges are available as the

polarizing field is increased accounting for increased charge with the increased field in accordance with equation (1) given above. When the photoelectret is excited by the radiation, the charges are released first from shallow and then from deep traps accounting for the initial faster decay followed by a slower decay.

It is clear from *Figure 2* that the charge released by the doped samples is greater than that released by the undoped PS. Moreover, there is a saturation at 3 kVcm^{-1} (9 V). This could be understood as follows:

The dopant acrylic acid has the structural formula:



It is an α - β unsaturated carbonyl compound. It possesses both C=C and C=O double bonds and exhibits the properties of these two functional groups. These double bonds act as deep traps for the electrons generated during the photoelectret formation of the doped samples. On re-irradiation these carriers are released from these traps accounting for the greater charge in the doped samples. As a charge transfer complex is formed between the PS matrix and the dopant AA²⁴, the charges take more time to be released from these traps, accounting for the slower decay for the doped samples. At high fields the increase in polarization is slowed down because of the saturation of the number of traps available. When all the traps are filled any excess electrons and holes will recombine rapidly, accounting for the saturation of charge with field, for the optimally doped samples. The saturation of Q with field in the optimally doped PS can also be understood from the compensation in the increase of carrier storing (in photo-polarization process) and emission centres (in the depolarization process) in the doped matrix, by the transfer of energy from one centre to the other which ultimately is dissipated at some defect centres, in the form of lattice vibrations (phonons) or structural defects²⁰.

It is found (*Figure 3*) that the photo-depolarization current and the charge of the doped and undoped samples increase with exposure time. This can be understood in terms of carrier trapping becoming more effective at higher illumination levels during the photo-electret formation and their subsequent release on re-irradiation, as the trapping probability is proportional to the product of trap-density and density of free carriers^{25,26}. Fridkin^{11b} further suggested that photo-polarization is a direct function of the exposure time and the absorption of photons in organic solids leads to photo-generation of charge carriers. The field effect is sensible approach when the dependence of polarization on time is taken into account. The build up of polarization with time in PS is characterized by an initial rapid increase. Due to doping this polarization behaviour becomes more pronounced. The dopant increases the number of charges generated in the doped samples first by C=O double bonds and subsequently releasing them on re-illumination. Their number increases with the exposure time and also gives rise to more charge in the doped samples, as observed here.

CONCLUSION

From the above discussion it may be concluded that the

doped polymers form better photo-electrets which retain their polarization for a longer time period.

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