Optical and Electrical Characteristics of Electrodeposited Polypyrrole Films

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SYNOPSIS

The optical and electrical properties of BF_4^- doped polypyrrole (PPY) have been studied in detail. The effect of annealing on the optical and electrical properties of BF_4^- doped PPY is reported. Interestingly, these properties are modified with annealing and it is observed that PPY is similar to other inorganic amorphous semiconductors. It is also seen that the electrical and optical properties of BF_4^- doped PPY are stabilized after 70 h of annealing at 70°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Conducting polymers such as polypyrrole, polythiophene, polyaniline etc., currently being investigated are considered to be the key to further progress in solid-state electronics. For example, both polypyrrole (PPY) and polythiophene have been used in the fabrication of solid-state electronic devices such as metal-semiconductor and metal-insulator-semiconductor FET structures because of the availability of a wide range of energy band gaps.[1-6] The operation of a solid-state electronic device and the requisite characteristics depend upon the barrier interface between the metal and the polymer, work function of the metal, and the band gap of the polymer. The electrical conductivity of a conducting polymer, which essentially depends upon mobility, magnitude of charge, and the defect concentration, is said to play an important role in the functioning of a given device. Further, the movement of polarons and bipolaronic defects along the polymeric chains is likely to affect the performance of such a device. It has now been suggested that most polymeric semiconductors contain mostly (90%) amorphous structures[7] and hence the general concepts of solid-state physics in amorphous states may be approximately valid for polymers.

Semiconducting polymers have an energy band gap that depends on the type of dopant, magnitude of defect concentration, and the structure of the polymer. The energy band gap of a conducting polymer gives information pertaining to optical, electronic, and electrical conductivity behaviour of the polymer. Information on band gap is very helpful in the determination of operational characteristics of a device. From the point of view of the performance of an opto-electronic device, essentially two factors are important: (1) the absorption of the incident optical radiation; and (2) the generation–recombination of the charge carriers that determines both the efficiency and the response time of an opto-electronic device. In general the values of these parameters can be modified by suitably doping the polymer to create defect states in the band gap that act as traps and recombination centres. The investigations of optical absorption near the band edge and the resulting absorption spectra impart important information relating to various processes occurring in conducting polymers. The polymers generally exhibit resonance absorption peaks in the IR region of the spectrum that have been attributed to the rotational, oscillatory, and vibrational movement of the molecules. Optical studies of BF_4^- and ClO_4^- doped PPY films in the IR region have been carried out.[8,9] The optical absorption studies in the range

of 400–2600 nm can lead to more information about the energy band gap of PPY films. In the higher frequency range, it is expected that information on transitions involving the movement of polarons, bipolarons, and the various states of the bound electrons associated with it, can be delineated.

The environmental, electronic, and mechanical stability of a device are essential factors in determining the performance of such a device. For the application of any device, the energy band gap, resistivity, and structure should remain nearly constant in different ambients and should not show any significant variation with time. With this as a motivation we have carried out studies on the effect of annealing on the resistance, surface morphology and optical absorption studies on BF_4^- doped PPY films. We report the results in the present paper.

EXPERIMENTAL

PPY films (thickness of the order of 2 μm) were prepared by electrodeposition techniques in solutions containing $0.1M$ pyrrole as the monomer, $0.1M$ tetraethylammonium-tetrafluoroborate as the supporting electrolyte, and acetonitrile containing 1 mL of water by volume as the solvent.[10] The reaction vessel consisted of a three electrode structure consisting of an indium-tin-oxide coated glass plate as anode, a platinum foil as cathode, and a standard calomel electrode as the reference electrode. The electrolyte and pyrrole were obtained from Fluka Chemic A.G. ITO glass plates with sheet resistance of 15–20 ohm/□ were prepared by vacuum deposition. The electrodeposition was carried out under isothermal conditions and inert atmosphere. Current densities of $\approx$ 8 mA/cm^2 (at 15 V) were used for the electrodeposition. The required polymeric films were obtained at the anode. For optical absorption studies, very thin films of PPY (of the order of 2000 Å) were prepared.

The conductivity of the films was measured using a four-points probe. Optical absorption measurements in the range of 400–2600 nm were carried out using a Hitachi U-3400 spectrophotometer. The optical absorption spectra were normalized taking into account the optical absorption of ITO coated glass plate as the reference. Annealing of the films was carried out at 70°C in vacuum for varying time intervals. For the measurement of resistance of the PPY films, electrical contacts of different PPY films were made by vacuum deposition of silver electrodes 1 cm apart. The surface morphology was investigated by scanning electron microscopy.

RESULTS AND DISCUSSION

The conductivity of doped polypyrrole films was found to be of the order of 5–10 ohm^{-1} cm^{-1}.

Figure 1(a) shows the optical absorption and transmission spectra of BF_4^- doped PPY films in the range of 400–800 nm. An absorption peak at 650 nm is apparent in this spectrum. This pattern in optical absorption is consistent with the optical absorption as observed in the case of polyacetylene.[9] It is evident that reflection from the surface of the PPY film is comparatively smaller. The absorption is at a minimum at 450 nm and increases as the wavelength is increased and has a peak at 650 nm while the transmission reduces as the wavelength is increased from 400 nm to 800 nm.

Figure 1(b) shows the optical absorption and transmission of BF_4^- doped unannealed PPY film in
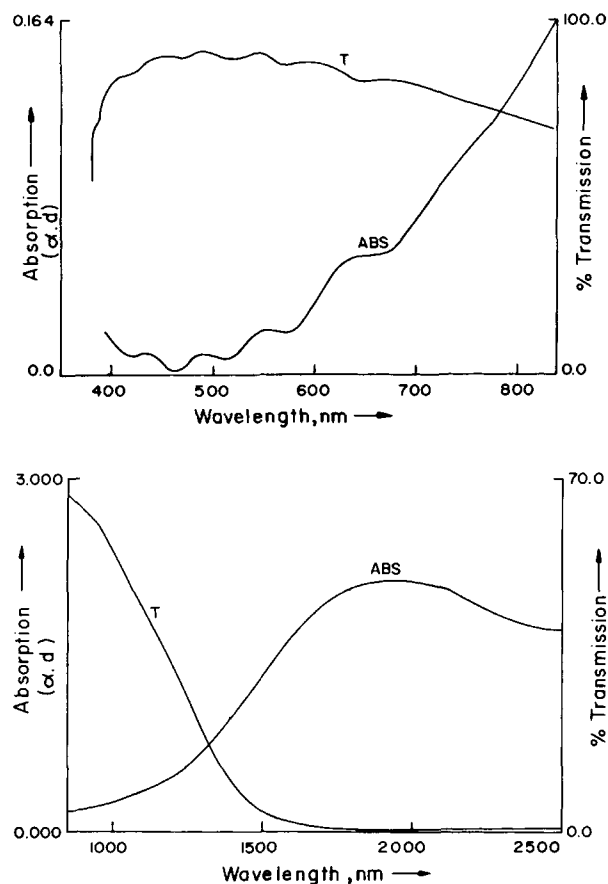
Figure 1 (a) Optical absorption and transmission of unannealed BF_4^- doped PPY films in the range of 400–900 nm. (b) Optical absorption and transmission of doped unannealed. PPY films in the range of 1000–2600 nm. Absorption = $\alpha \cdot d$, where α = absorption coefficient and d = thickness.

the range of 1000–2600 nm. The optical absorption increases as the wavelength is increased to about 800 nm showing a peak around 2000 nm. This peak is attributed to the rotational and vibrational modes of molecules. The transmission in this range reduces to the wavelength of 1500 nm after which it is almost nil. Other conducting polymers show a similar behaviour.

The optical absorption $\alpha \cdot d$ in conducting polymers is propositional to $(h\nu - E_g)^{-1/2}$ as these are one-dimensional lattices (since the electron energy band and the energy band gap are one dimensional) where $h\nu$ is the incident photon energy and E_g is the energy bandgap. The density of states $g_{h1}(E)$ is given by

$$g_{h1}(E) = \frac{L}{\Pi}\,(\nu/2)^{1/2} \cdot \frac{1}{h} \cdot \left(\frac{1}{h\nu - E_g}\right)^{1/2}$$

indicating that $(\alpha \cdot h\nu)$ is proportional to $\left(\dfrac{1}{h\nu - E_g}\right)^{1/2}$.[11] An estimate for E_g can be obtained by plotting $(1/\alpha \cdot h\nu)^2$ vs. the photon energy. A strong singularity can be seen around the band-gap E_g.

Figure 2 shows a plot of $(1/\alpha \cdot h\nu)^2$ vs. photon energy for unannealed BF_4^- doped PPY. The optical

absorption edge as determined from Figure 2 is seen to be around 2.7 eV. The optical energy band gap has been estimated to be $E_g = 3.0$ eV. The absorption peaks observed in the absorption versus photon energy plot can be attributed to various polaronic and defect levels. However, these structures seem to be smeared out in Figure 2. These levels also distinctly appear in the reflection spectra of BF_4^- doped PPY films. These defects levels are degenerate and localised within the energy band gap. In conducting polymers, which have amorphous structure, band edges are not very sharp and the energy band gap can only be assumed to be an apparent band gap. The absence of crystallinity in the doped PPY makes the band edges blunt as in the case of amorphous semiconductors and the band edges contain tails with reasonable density states.[12] This may cause the energy band gap to vary within a range. The observed peak in the absorption spectrum at around 0.9 eV is analogous to the 1.0 eV peak in ClO_4^- doped PPY films dependent upon the doping concentration and hence can be attributed to the trapping sites created by the doping.[13,14] It has been reported that the band gap of PPY lies in the range of 1.4–6.0 eV depending upon the process used for the preparation of the films and the type of dopants.[15,16] The chains in PPY consist of $\alpha - \alpha'$ bonded pyrrole units rotated by 180° and every ring is related to its neighbour by screw symmetry and contains 2Π electrons; the nat-
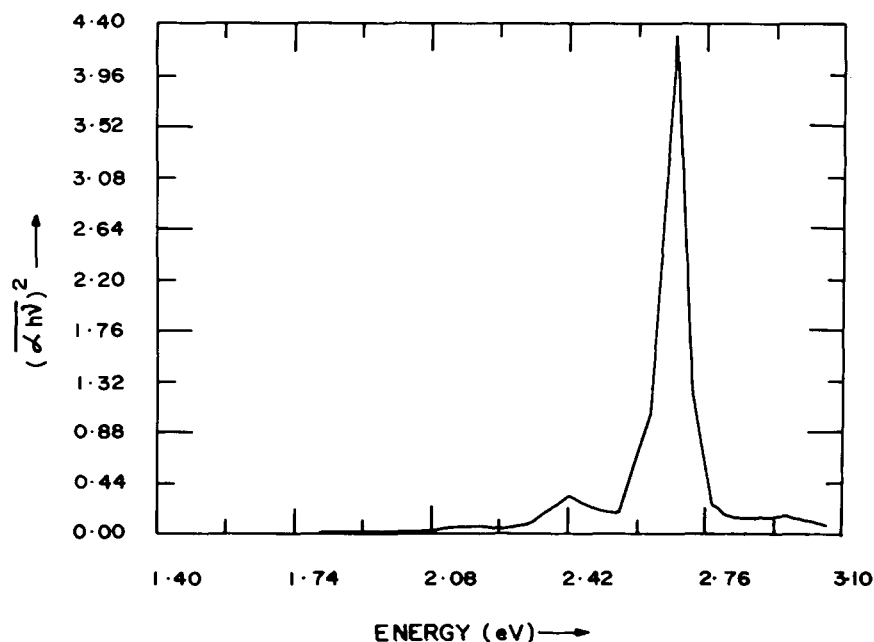
Figure 2 Plot of $(\alpha \cdot h\nu)^{-2}$ vs. photon energy for unannealed BF_4^- doped PPY films in the range of 1.4–3.1 eV.

ural PPY is semiconducting having a band gap of 3.2 eV.[17,18] However, doped PPY is known to be highly disordered and has an energy band gap of 2.70 eV.

Figure 3 shows the variation of resistance as a function of annealing time when the BF_4^- doped PPY films are annealed at 70°C. The resistance of the BF_4^- doped PPY film increases sharply with time within the initial 15 h of annealing, reaching a peak value of 56 $\Omega/\square$ and decreases steadily to about 12 $\Omega/\square$ after continuous annealing of 25 h. Further annealing of these PPY samples does not result in any change in the resistance that stabilises at about 12 $\Omega/\square$. The initial increase in the resistance of the doped PPY film may perhaps be caused by the evaporation of the solvents from the films during the annealing process. Due to the complex structure of the polymeric chains in the electrochemically deposited PPY films, polymeric molecules are locked in the resulting structure. This restructuring of the PPY films leaves voids and pores that act as resistive paths. This process is completed within 15 h of annealing. Further annealing results in the restructuring of the PPY films eliminating the persistent voids and pores, which in turn, results in the decrease of resistance. After annealing for 40 h, the resistance attains a stable value. This indicates that a complete ordering of the polymeric chains has occurred leading to a stabilised polymeric structure.

The SEM micrography (Fig. 4) of unannealed BF_4^- doped PPY film shows a continuous and uniform surface morphology embedded in a uniform medium. Figure 4(b) shows the surface morphology after annealing for 15 h at 70°C. The surface morphology reveals the above stated restructuring of the film. This perhaps gives rise to the maximum value of the resistance of the doped PPY film. Further, a large number of voids and pores are observed in Figure 4(b). Figure 4(c) shows the surface morphology of the above PPY film after it has been annealed for 40 h. Interestingly, uniform structure containing no voids and pores is visible in Figure 4(c). The continuous uniform distribution of doped PPY electrodeposits perhaps yields a minimum value of resistance. Figure 4(d) shows the surface morphology of the above PPY film after annealing for 100 h. It shows that, even though the resistance of the film after annealing at 70°C for 100 h become stabilized, the surface morphology no longer remains smooth [Fig. 4(c)].

The optical properties of BF_4^- doped PPY are modified with annealing. This is expected for an amorphous solid. Figure 5 depicts optical absorption of BF_4^- doped PPY films annealed to various levels.
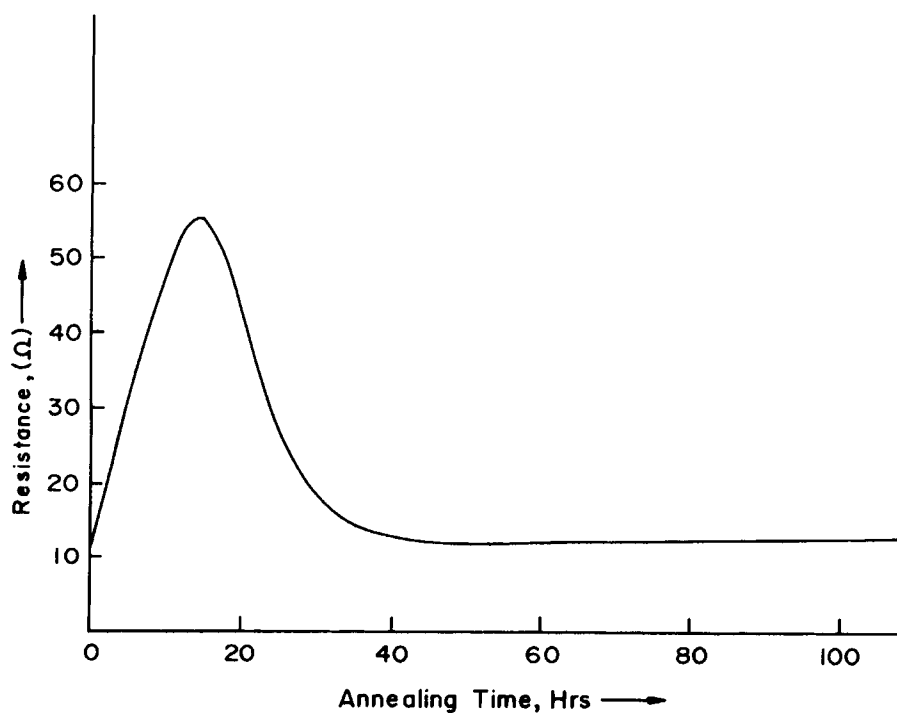
Figure 3 Plot of resistance vs. annealing time for BF_4^- doped PPY films, annealing temperature 70°C.
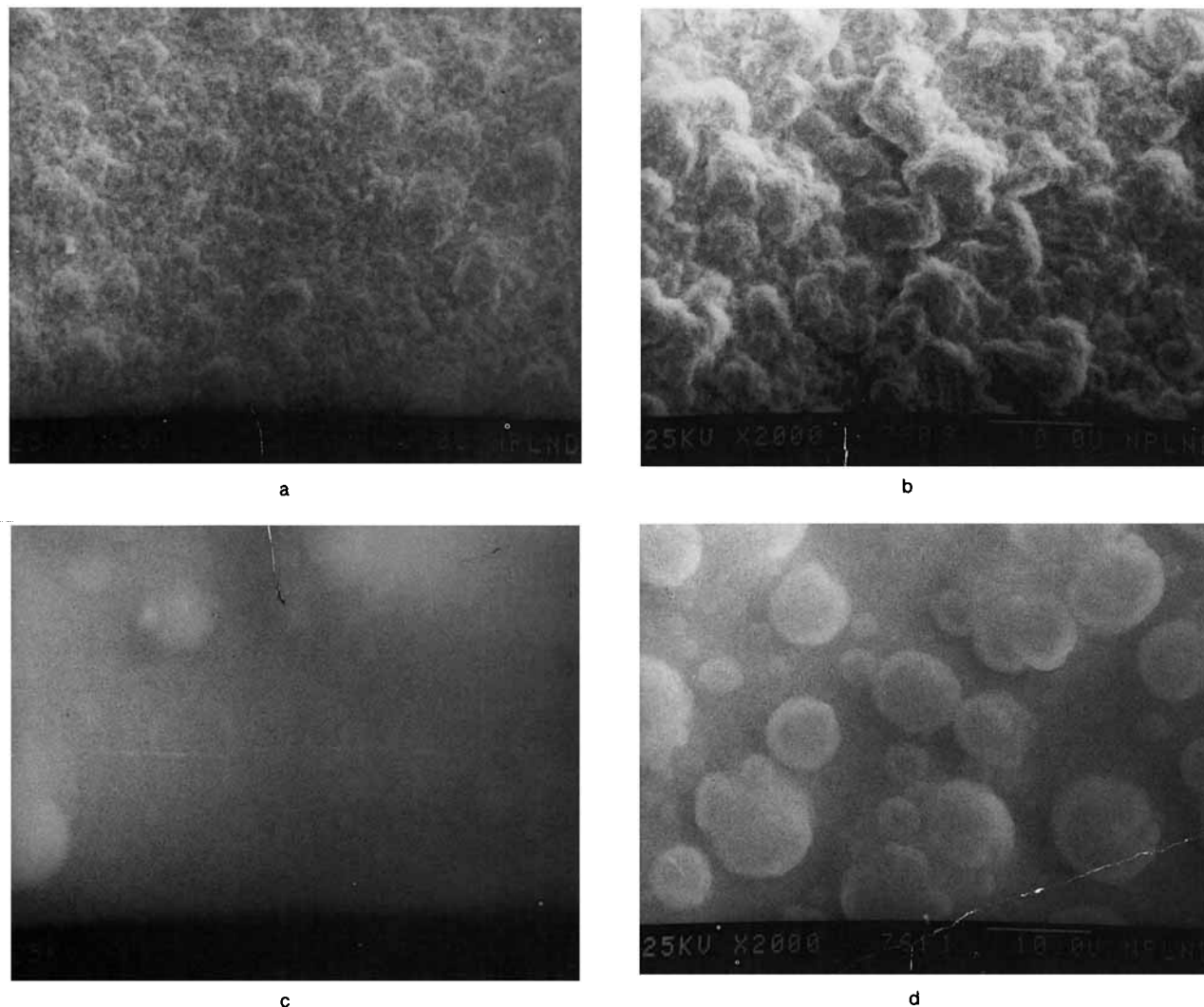
Figure 4   Scanning electron micrography of doped PPY films (a) unannealed, (b) annealed 15 h, (c) annealed 40 h, (d) annealed 100 h; annealing temperature 70°C.

The peak in the region of 1000–2600 nm is usually attributed to the polaron defect levels that determines the conductivity properties of PPY. That the band tails do show significant modification upon annealing is clearly seen in Figure 5.

CONCLUSIONS

These studies indicate that BF_4^- doped films exhibit optical absorption in the range of 400–2600 nm. The optical peak absorption is observed at around 650 nm. The energy band gap as determined by the optical absorption studies has been found to be E_g =3.0 eV. The value of the energy band gap depends upon the carrier concentration in the conducting polymer, which in the case of PPY has been found to be of the order of $10^{20}/cm^3$ as in our earlier observations.[5] Further, the resistance of the BF_4^- doped PPY films exhibits a transition during annealing at 70°C attributed to the structural changes in the PPY films as revealed by scanning electron microscopic studies. These structural changes are perhaps caused by the evaporation of the solvent from the film resulting in the creation of voids and pores. The annealing of PPY films essentially triggers the process of filling of such voids and pores. Thus after 40 h of annealing the resistance has stabilised and the PPY film becomes electrically stable. The modification of optical properties upon annealing is also observed.
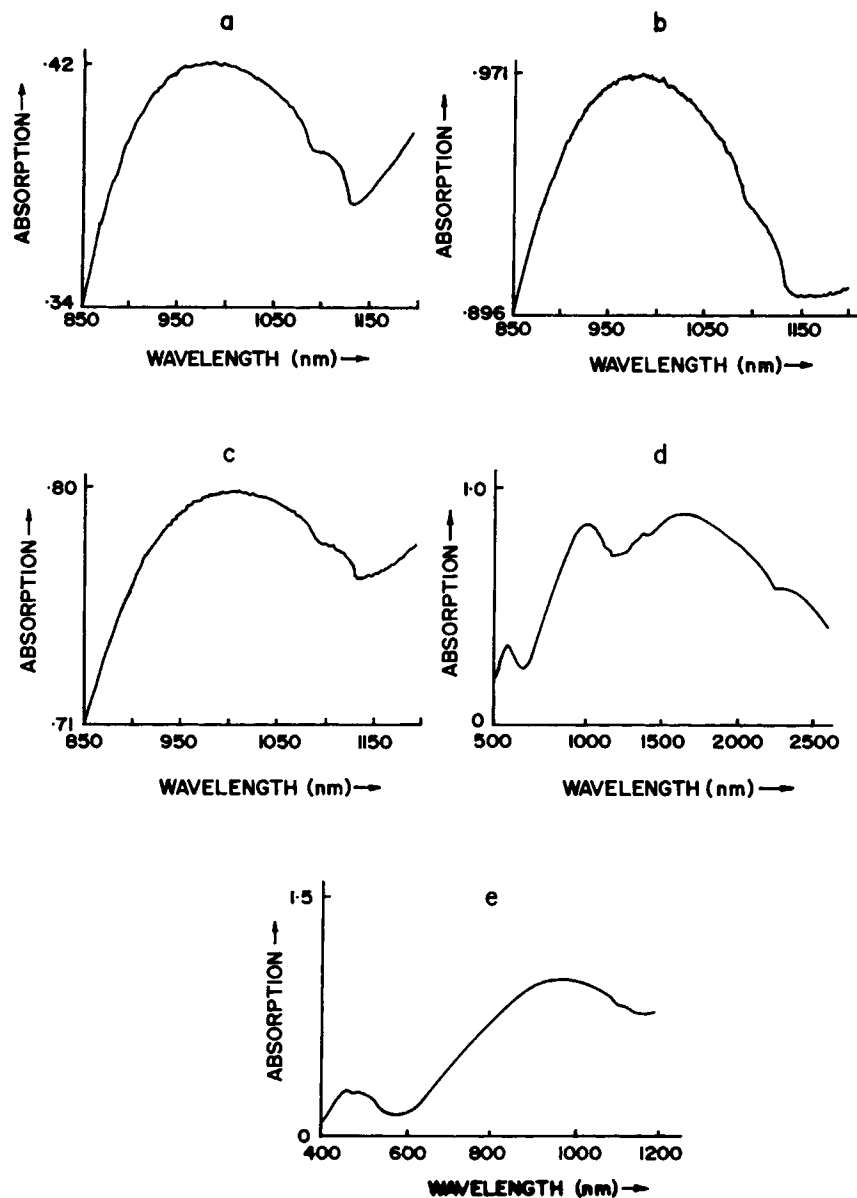
Figure 5 Optical absorption of BF_4^- doped PPY films in the range of 1000–2600 nm (a) annealed 20 h, (b) annealed 40 h, (c) annealed 70 h, (d) annealed 70 h, (e) annealed 100 h.

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