Charge and discharge of organic dye-doped polymeric matrix

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Copper–phthalocyanine has been dispersed in polystyrene matrix to prepare the rigid glasses and their electrical properties have been investigated by studying the temperature dependence of conductivity and observing the thermally stimulated discharge current spectra. Increase in conductivity of the polymer is assigned to the presence of dopant molecules affecting the carrier mobility. The large space charge polarization observed confirms this fact.

INTRODUCTION

Knowledge of energy transfer may be gained by studying the variation in electrical conductivity with temperature and by analysing the thermally stimulated discharge current (*TSDC*) spectra. Electrical spectroscopy (*TSDC*-technique) has proved to be especially well suited to characterize the polymers[1]. *TSC* spectra are very sensitive to additives, impurities and humidity, i.e. to any chemical or morphological change, so this technique may well be used to study the doping effects. Polystyrene (PS) is chosen for the present investigation because it is a comparatively rigid-chain nonpolar polymer[2] and its bulk structure is relatively well known. Thermoluminescence[3] and *TSD*[4] experiments on PS films have revealed a peak in the main relaxation region of the polymer (100–110°C) due to detrapping of charge carriers. Properties of phthalocyanines (an important class of organic dyes) have been investigated extensively in reported literature[5–7]. Copper–phthalocyanine (Cuph) has been selected as a material to be dispersed in PS-matrix. This paper expands on temperature variation of conductivity and *TSD* of Cuph doped PS films.

EXPERIMENTAL

Cuph dissolved in concentrated sulphuric acid was added dropwise into the polymer solution in cyclohexanone while stirring. Films were grown on cleaned Al-substrates by the isothermal immersion technique. Film thickness was determined by measuring its capacitance at 10 kHz and using a dielectric permittivity of $\varepsilon = 3$. All films were $\sim 20\ \mu$m thick. No signs of crystallization under ambient conditions could be noted in the concentration range used. The substrate acted as an electrode while that of Al (1 cm^2 in area) was sandwiched on the film. A Keithley 600B electrometer was used to read the current. The charging current was measured by applying a d.c. voltage and heating the sample at a rate of 1° min^{-1}. The *TSC* spectra of films were observed under identical conditions of voltage, time and heating rate. All the experiments were performed in air.

RESULTS

The conductivity (σ) was evaluated from the measured value of current. The conductivity curves (σ vs. $10^3/T$) of pure and Cuph doped PS films are shown in *Figure 1*. The activation energy (E) was calculated from Arrhenius relation:

$$\sigma = \sigma_0 \exp\left(\frac{E}{kT}\right) \qquad (1)$$

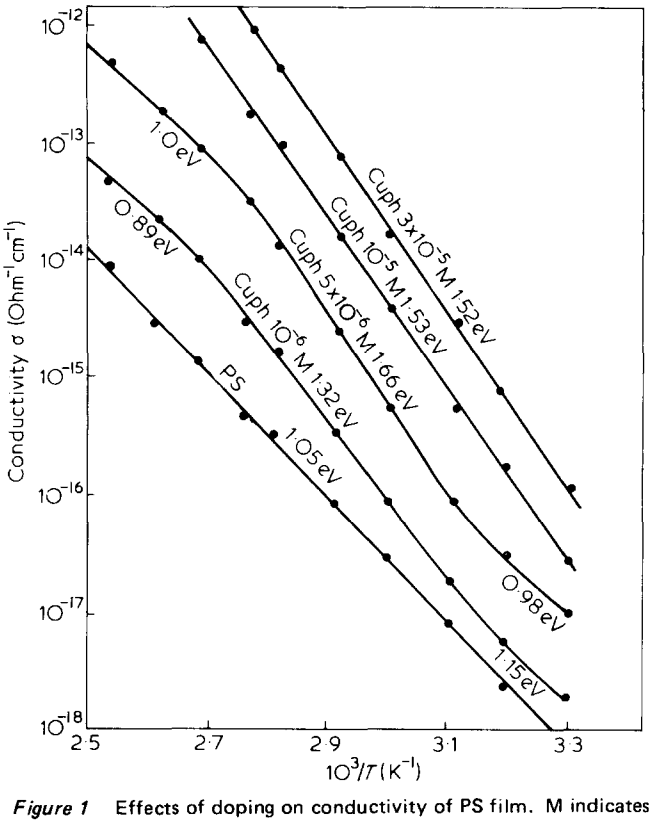

Figure 1 Effects of doping on conductivity of PS film. M indicates molar concentration

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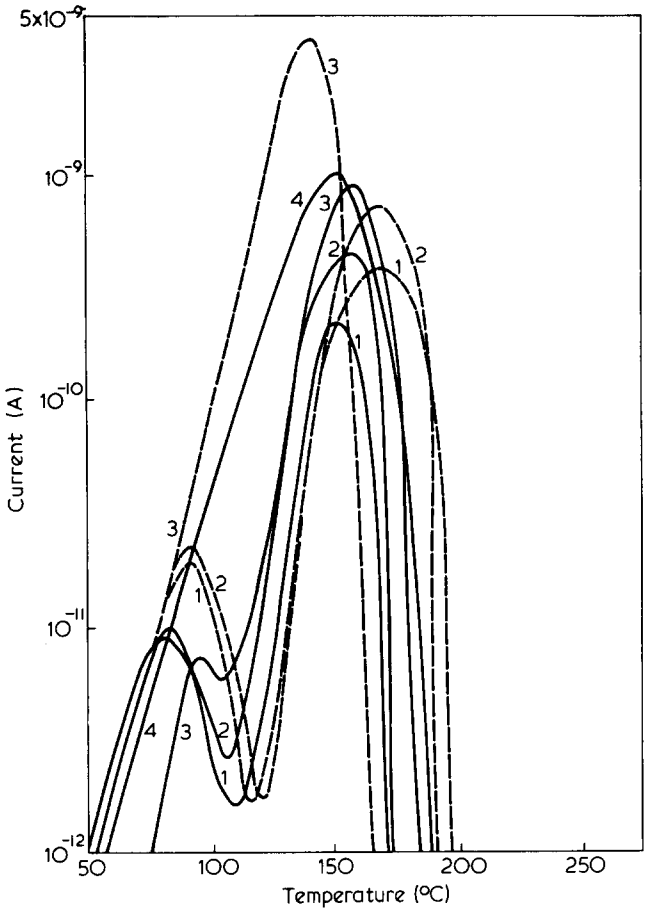

Figure 2 Effect of poling temperature on *TSC*-spectra of Cuph-doped PS films. (– – –), 7×10^{-5} M; (——), 1.4×10^{-5} M; 1 = 70°C; 2 = 80°C; 3 = 90°C; 4 = 105°C

where σ_0 is a constant and k is Boltzmann's constant. The conductivity of PS film increases linearly with temperature and has $E = 1.05$ eV. The conductivity curve of PS film doped with 10^{-6} M Cuph has three regions in the temperature ranges 30–50, 50–90 and 90–120°C whose activation energies are 1.15, 1.32 and 0.89 eV respectively. Increase in concentration of Cuph makes three regions more pronounced and the activation energies of these three regions at 5×10^{-6} M are 0.98, 1.66 and 1.0 eV respectively. Further increase in the dopant concentration brings three regions to terminate into one and at 10^{-5} and 3×10^{-5} M Cuph, the activation energies come out to be 1.53 and 1.52 eV respectively.

Full line curves numbered as 1, 2, 3 and 4 in *Figure 2* are the *TSC*'s released from the films doped at 1.4×10^{-5} M and poled at 70, 80, 90 and 105°C respectively. The curves 1, 2 and 3 are made of two peaks. The first peak in all the curves occurs at a temperature which is lower than the glass-transition temperature of PS while the second peak arises well above the glass-transition of the polymer. Curve 4, obtained by poling the film at 105°C, consists of only one peak. The dotted curves of *Figure 2* numbered as 1, 2, and 3 are the TSC spectra of films doped at 7×10^{-5} M and poled at 70, 80 and 90°C respectively. The spectra 1 and 2 contains two peaks, one below and the other well above the glass-transition of PS while the spectra 3 has only one peak. The activation energy H of the discharge process was calculated from Grossweiner's formula[8]:

$$H = \frac{1.3 \times 10^{-4} T_m T_h}{T_m - T_h} \qquad (2)$$

where T_m is the peak temperature and T_h is the temperature corresponding to the half height of the peak on the lower temperature side of the spectrum. Natural relaxation time Γ_0 was estimated from:

$$\Gamma_0 = \frac{k T_m}{B H \exp\left(\frac{H}{kT}\right)} \qquad (3)$$

where B is the heating rate. TSC parameters are listed in *Table 1*.

DISCUSSION

The low temperature tail below 50°C in conductivity curves of the doped films may be attributed to impurity conduction with low activation energy. Above 50°C high activation arises from intrinsic conduction. Around 90°C a bend occurs before the glass-transition temperature of PS. The difference in activation energies is due to higher dissociation energy to form the carriers for intrinsic conduction. Gupta[9] has also observed similar types of results with poly(vinyl fluoride) due to doping. Incorporation of higher ciocentrations (e.g. 10^{-5} and 3×10^{-5} M) of Cuph reveals a decrease in activation energy in the temperature range 50–90°C. The conductivity is increased considerably, which may be associated with the increase in mobility due to doping[10]. The values of activation energies are high and so carrier hopping is not possible. This suggests a transport process directly analogous to the thermally assisted trapping and release motion described by Spear *et al.*[11]. The carrier is raised to a level above its initial trapped state and then moves in that level until retrapping occurs. The guest molecules are undoubtedly responsible for the presence of deeper traps, while defects of the chain structure give rise to shallow traps. The trapping activity of the guest molecules depends on their electron affinities and ionization potentials. The shallow traps are those from which carriers are released thermally and deep trapping levels occur where charge carriers stay longer.

What has been said above is also confirmed from the *TSD* measurement. *TSC* spectra of the doped films have been observed to exhibit α and ρ peaks in contrast to the α peak alone of pure PS[4]. Polymer chain motions are

Table 1 *TSC* parameters

Poling temperature (°C)	Peak temperature (°C)	Activation energy (eV)	Relaxation time (S)
	7×10^{-5} M Cuph doped PS		
70	90	1.71	7.3×10^{-23}
	180	3.01	9.9×10^{-33}
80	92	1.47	2.0×10^{-19}
	170	2.83	1.6×10^{-31}
90	142	1.40	9.6×10^{-14}
	1.4×10^{-5} M Cuph doped PS		
70	82	0.71	5.2×10^{-9}
	158	1.92	1.4×10^{-21}
80	85	1.13	5.2×10^{-15}
	152	2.19	3.7×10^{-25}
90	95	1.81	4.7×10^{-24}
	155	1.61	4.9×10^{-18}

involved in the origin of the α peak while the ρ peak arises well above the glass-transition of PS due to the charges which take part in conduction mechanism. The charges may be ions or electrons and may originate from the dissociation of the dopant molecules. The intensities of the current maxima are larger than those expected according to the linear mixing rule of heterogeneous structures[1,2]. Doping creates new trapping sites in the rigid matrix. The presence of marked space charge polarization leads to conclude that incorporation of Cuph in PS enhances its conductivity. Since it is necessary for the occurrence of the ρ peak that there be enough carriers of sufficiently high mobility, the increasing conductivity of the polymer due to doping is mainly due to the increase in mobility of the carriers. Increase in the dopant concentration at a fixed poling temperature, and the increase in poling temperature at a fixed Cuph concentration, causes α and ρ peaks to degenerate into one because both the factors enhance the conductivity of the polymer making it accumulate more space charge.

CONCLUSION

Doping of the PS matrix with Cuph enhances the conductivity of the polymer. The increase in conductivity is due to the increase in mobility of charge carriers due to impregnation of the matrix. Addition of Cuph greatly enhances the intensities of the *TSD* current peaks especially of the ρ peaks due to increase in conductivity of PS. This magnification of intensity is more than that expected according to the linear mixing rule of heterogeneous structures.

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