Electrical conduction mechanism in poly(vinyl pyrrolidone) films

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The electrical conduction mechanism in poly(vinyl pyrolidone) films sandwiched between planar aluminium electrodes has been investigated. The films were obtained by the solution growth technique and the thickness was measured to be 17.6 μm. The electrical conduction and current–voltage characteristics were investigated in the temperature range 300–452 K with both symmetric and asymmetric electrode configurations. Hysteresis in the I–V characteristics was observed. The results were interpreted in terms of a Poole–Frenkel type conduction mechanism operating over the entire range of temperature and field strength.

(Keywords: electrical conduction; poly(vinyl pyrrolidone) films; Poole–Frenkel mechanism)

INTRODUCTION

Studies of the transport mechanisms in polymer films have gained importance in recent years owing to potential applications of films in various device technologies[1]. The nature of possible conduction mechanisms has not yet been fully understood, despite many efforts by various workers[2–19] on a large number of polymers, probably because of the highly disordered structure and high molecular weights of polymers. However, a variety of polymers have yet to be explored, so we have made an attempt to understand the nature of the conduction mechanism in poly(vinyl pyrrolidone) polymer films by studying the conductivity and current–voltage–temperature characteristics.

EXPERIMENTAL

Poly(vinyl pyrrolidone) of molecular weight *ca.* 40 000 (supplied by SISCO Research Laboratories Ltd., Bombay) was used in the present investigations. Films of thickness 17.6 μm were grown by the isothermal immersion technique[20] from the aqueous solution of the polymer on aluminium substrates at room temperature. Films were dried in vacuum for 48 h at a temperature well below the soft temperature. The thickness was estimated by gravimetric and capacitance methods, which were found to be in good agreement with each other.

Electrical conduction was studied in a sandwich configuration. The substrate itself acted as one of the electrodes and the other, an aluminium electrode of area 1 cm^2 was vacuum evaporated on the polymer film by using a suitable mask. The top aluminium electrode was pressed against the evaporated electrode with the help of a screw. A copper–constantan thermocouple was placed very near the experimental film to monitor temperature. Films were heated in an evacuated and electrostatically shielded vessel.

The films were annealed before measurements were made. In this annealing process, the film was heated from room temperature to 425 K, while the conductivity was monitored regularly. The process of heating and cooling was repeated on the film a number of times, until reproducibility in the conductivity was obtained.

The conductivity of the film was evaluated as a function of temperature by measuring current, with an electrometer amplifier (EA 815), when a constant voltage was applied across the film. The current–voltage characteristics were studied at different temperatures (305, 331, 357 and 377 K) in the usual manner. The thermally stimulated discharge currents were also studied at different polarizing field strengths (114, 341, 568, 1136 and 2272 kV m^{-1}) and polarizing temperatures (305, 314 and 323 K).

RESULTS AND DISCUSSION

The current as a function of temperature in the range 300–425 K was measured at an applied field strength, F, of 0.57 MV m^{-1} and the conductivity of the films was evaluated. The unannealed films initially showed high conductivity (6.85×10^{-11} S m^{-1}), but it decreased with the number of annealing cycles until it finally demonstrated reproducibility. This decrease in conductivity with annealing may be attributed to the partial crystallization of polymer films[21]. Similar behaviour was reported by Bahri and Singh[22] on poly(vinyl chloride) films.

Figure 1 shows the variation of log (I/T^2) as a function of $1000/T$ for well-annealed films. The conductivity of the films at room temperature was found to be 3.9×10^{-14} S m^{-1}. Conductivity was also studied as a function of the applied field in the same temperature range, but the field was found to be negligible. The general variation of conductivity with temperature is similar to that for other polymers, poly(vinyl formal)[19] and poly(vinyl chloride)[7,18]. From the slope of the graph log I *versus* $1000/T$, the activation energy was evaluated (0.62 eV).

The current–voltage characteristics of poly(vinyl pyrrolidone) films at different constant temperatures are plotted in *Figure 2*. At all these temperatures log I

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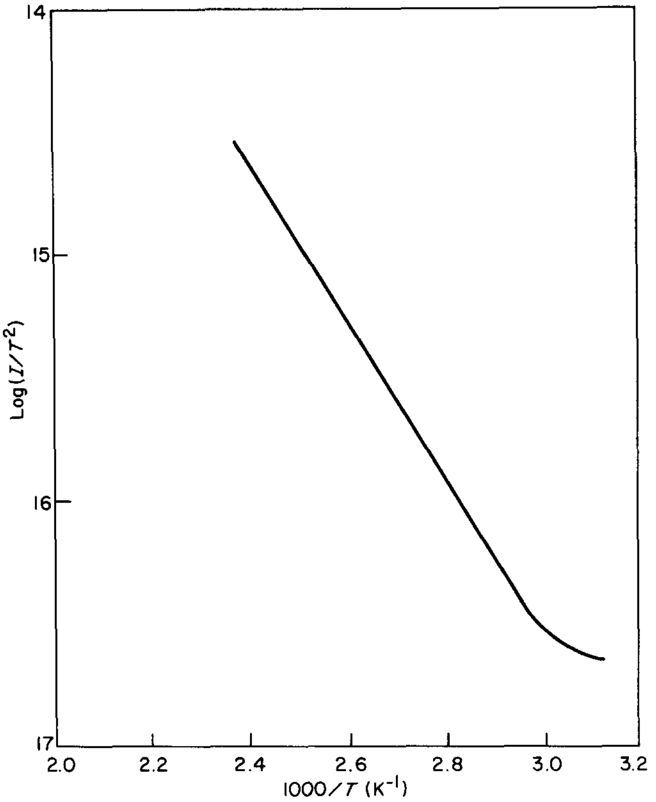

Figure 1 Variation of $\log(I/T^2)$ with $1000/T$

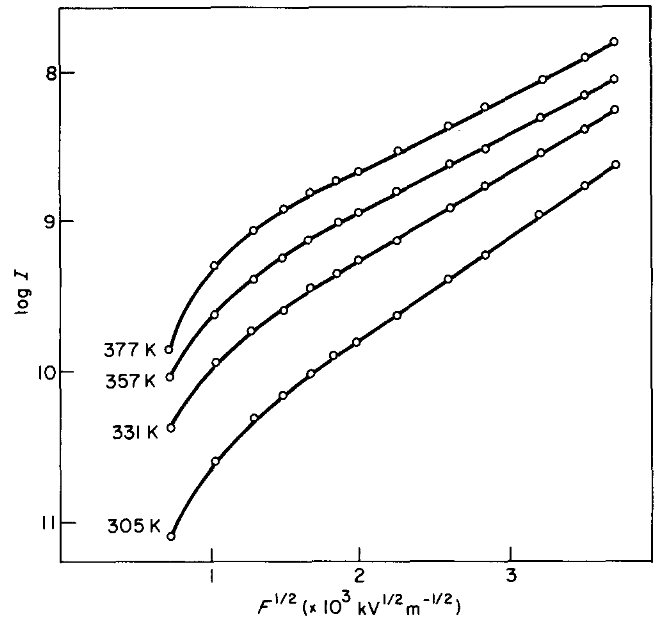

Figure 2 Variation of $\log I$ as a function of field strength at different temperatures

demonstrated a linear behaviour with $F^{1/2}$ at higher field strengths, but an appreciable deviation from linearity at lower fields. This deviation from linearity may be explained by accumulation of space charge at the electrodes[11].

The observed variation between current and electric field strength ($\log I$ *versus* $F^{1/2}$) suggests a conduction mechanism in which charge carriers are released by thermal activation over a coulombic potential barrier that is decreased by the applied electric field. The physical nature of such a potential barrier can be interpreted in two basic ways. It can be considered as a transition of electrons over the barrier between the cathode and dielectric, taking the classical imaginary force into consideration (Schottky emission). Alternatively, charge carriers can be released due to ionization of impurity centres in the dielectric (Poole–Frenkel effect).

To determine the actual conduction mechanism the values of β at different temperatures deduced from the slopes of the plots of $\log I$ *versus* $F^{1/2}$ are compared with theoretical values in *Table 1*.

The theoretical value of β may be deduced from the relation

$$\beta_{\mathrm{PF}} = 2\beta_{\mathrm{RS}} = 2[e/4\pi\varepsilon\varepsilon_0]^{1/2}$$

where ε is taken to be 3.7. The experimental value of β is in good agreement with β_{PF}. So it may be concluded that the Poole–Frenkel type of conduction mechanism is dominant in the present investigations.

However, the mere coincidence of β values may not be sufficient evidence to detect the conduction mechanism[23,24]. The actual conduction mechanism may be better determined by the effect of different electrode materials on the current–voltage characteristics, since the Richardson–Schottky mechanism is electrode-dependent whereas that of Poole–Frenkel is not[25]. Also, a study of thermally stimulated discharge currents as a function of polarizing field strength determines the actual conduction mechanism[26].

Figure 3 shows the current–voltage characteristics of poly(vinyl pyrrolidone) films at 305 K for different top-electrode materials. It is clear from the plot that the effect of different electrode materials on the current–voltage

Table 1 Theoretical and experimental values of β

Temperature (K)	Experimental $10^5\ \beta\ (\mathrm{V}^{1/2})$	Theoretical	
		$10^5\ \beta_{\mathrm{RS}}\ (\mathrm{V}^{1/2})$	$10^5\ \beta_{\mathrm{PF}}\ (\mathrm{V}^{1/2})$
305	3.75	1.97	3.94
331	3.68		
3.57	3.68		
377	3.56		

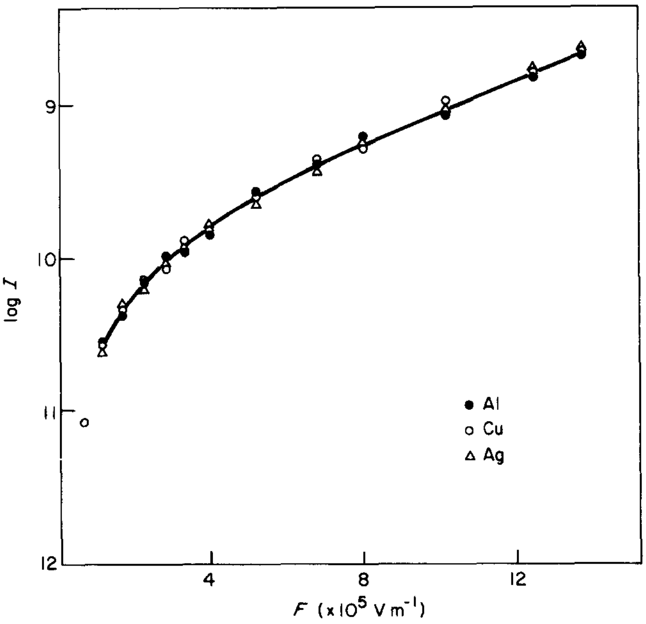

Figure 3 Variation of $\log I$ as a function of voltage at 305 K for different electrode materials

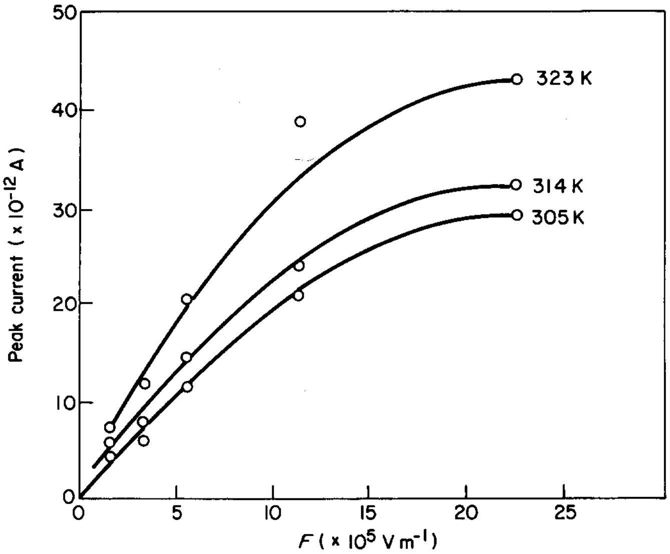

Figure 4 Variation of t.s.d.c. peak current with polarizing field strength for a heating rate of 0.14 K s^{-1}

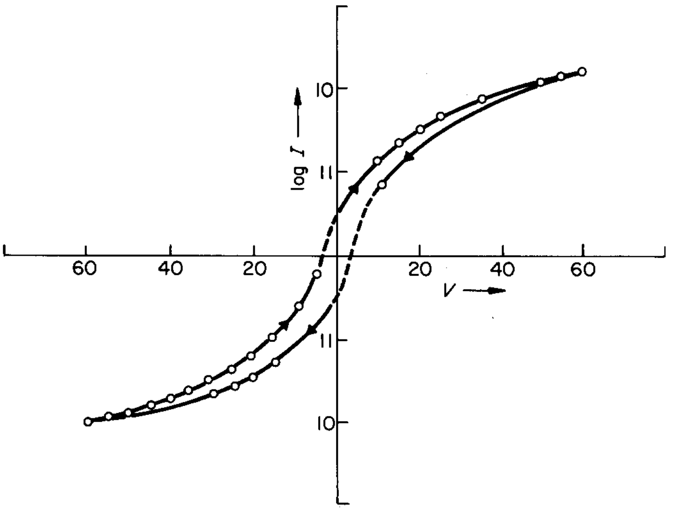

Figure 5 Current as a function of increasing and decreasing voltage

characteristics is negligible within the experimental errors, confirming that the Poole–Frenkel mechanism is the dominant one.

In the t.s.d.c. studies, the peaks may be due to disorientation of dipoles or migration of space-charge carriers over microscopic distances, released from the traps, with subsequent trapping. If the trapping centres are of a Poole–Frankel type, the temperature corresponding to the t.s.d.c peak is dependent on the polarizing field strength[27]. In the present investigations it was observed that the temperature corresponding to the peak was indeed a function of field strength, as seen in *Figure 4*.

The hysteresis of the I–V characteristics is shown in *Figure 5*. This hysteresis phenomenon implies that there was some standing voltage in the film, which could be the result of polarization.

CONCLUSIONS

In the process of annealing, a decrease in conductivity may be attributed to partial crystallization. The conductivity of poly(vinyl pyrrolidone) films was found to increase with temperature in a manner similar to an intrinsic semiconductor.

The I–V characteristics of pure poly(vinyl pyrrolidone) films with symmetric and asymmetric electrode configurations and t.s.d.c. studies confirm that the Poole–Frenkel type of conduction is the dominant one in the temperature range studied here.

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