A COMPARISON OF THE CURRENT-VOLTAGE CHARACTERISTICS OF COBALT, NICKEL AND LEAD POLYMETHACRYLATES

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SUMMARY: The electrical conductivities of transition metals namely, cobalt, nickel and lead polymethacrylates determined experimentally have been compared. The polymers were synthesized by free radical solution polymerization. These polymeric salts act as semi-conducting materials. The electronic mode of conduction determined from the experimental results has been discussed to elaborate the mechanism of conduction.

Key Words: Metal polymethacrylates, conductivity, semiconductors, ohmic character.

INTRODUCTION

Polymers typically have very high electrical resistivity and dielectric strength (1). However, through chemical syntheses, it is possible to achieve both chemical stability and a wide range of electronic properties. A new class of conducting polymers classified as metal polymethacryslates has emerged in recent years. Electrical properties of various metal polymethacrylates have been reported (2-6).

A major obstacle to the rapid development of conducting polymers is the lack of understanding of how the electrical current passes through them. Hence the primary research goal in this field is to understand the relationship between the chemical structure of polymer repeat units and its electrical properties. This provides an insight in to the electronic and mechanical properties of these materials. In this paper the electrical conductivities and the mechanism of conduction operative in cobalt, nickel and lead polymethacrylates have been discussed and compared.

MATERIALS AND METHODS

SYNTHESIS OF POLYMERS

Metal polymethacrylates were synthesized (5.7) by initially polymerizing 25% w/v of methacrylic acid (PMAA) in methanol at 60°C using azo-bis isobutyronitrile as initiator. The reaction was stopped after 120 minutes by pouring the mixture in to stirred dried diethyl ether. The solution of PMAA was mixed with methanolic sodium hydroxide to obtain white gelatinous sodium polymethacrylate. Water soluble sodium polymethacrylate was treated with aqueous solutions of the respective metal acetates in 1:0.5 molar ratios to precipitate the transition metal polymethacrylates. The polymer samples were dried at 40°C in a vacuum oven for 24 hours and stored in a desiccator.

ELECTRICAL MEASUREMENTS

Pellets of the polymer samples were prepared on a hydraulic press at room temperature. These pellets were 0.5 mm thick and 1 cm in diameter. The pellets were kept in an oven for 24 hours before depositing silver electrodes on both sides of the sample (3).

The arrangement for electrical measurements is shown in Figure 1. The sample holder is enclosed in a shielded ceramic cell. The temperature in the cell is kept constant by using a temperature controller. The current flowing in the sample is deter-

Figure 1: Experimental arrangement for electrical measurements.

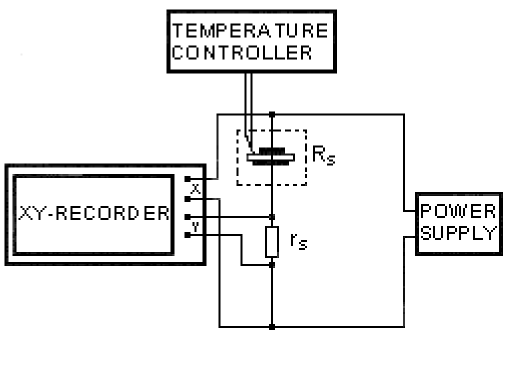

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Figure 2: Current vs. voltage at various temperatures for CoPMA.

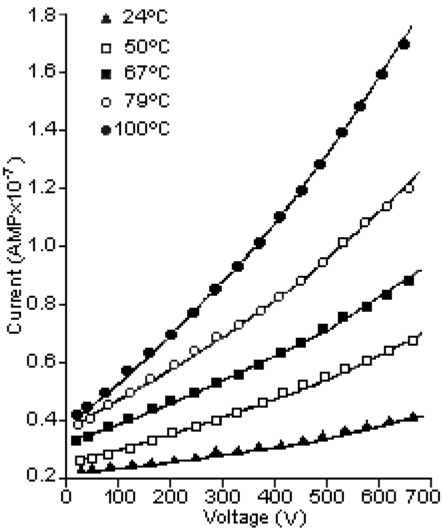
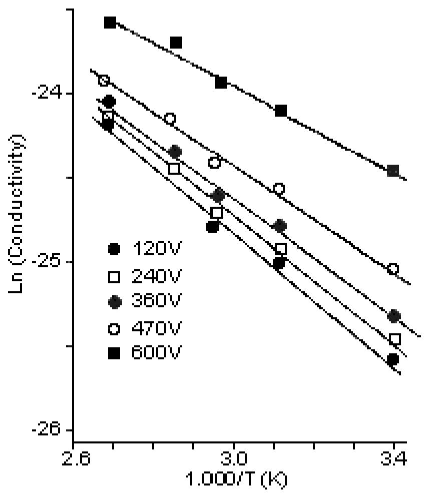


Figure 4: Plot for calculating activation energy (CoPMA).



mined by the voltage drop across a standard resistor measured on XY-recorder. In order to prevent current limiting, the standard resistor is always selected 2 to 3 orders of magnitude smaller than that of the sample resistance (8).

RESULTS AND DISCUSSION

The I-V characteristics of CoPMA are shown in Figure 2. It is evident from this figure that the sample follows Ohmic character at low voltage i.e., <300V beyond which an exponential rise in current is observed. This exponential dependence of current on voltage indicates a uniform density of traps (9). If the density of traps is assumed to be at discrete levels then this exponential rise in current can be interpreted as the "trap filled limit voltage". A linear relationship is obtained when log1 is plotted against V 1/2 (Figure 3). This behavior is associated with Poole-Frenkel conduction mechanism (10). According to this mechanism, the barrier for thermal excitation of trapped electrons between a metal contact (anode) and the conduction band of insulator/semiconductor (cathode) is lowered.

Figure 3: Log I vs. $V^{1/2}$ for CoPMA.

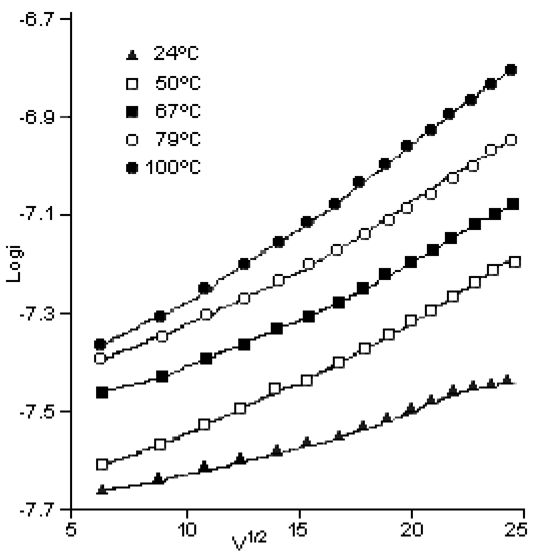


Figure 5: I-V relationship for NIPMA.

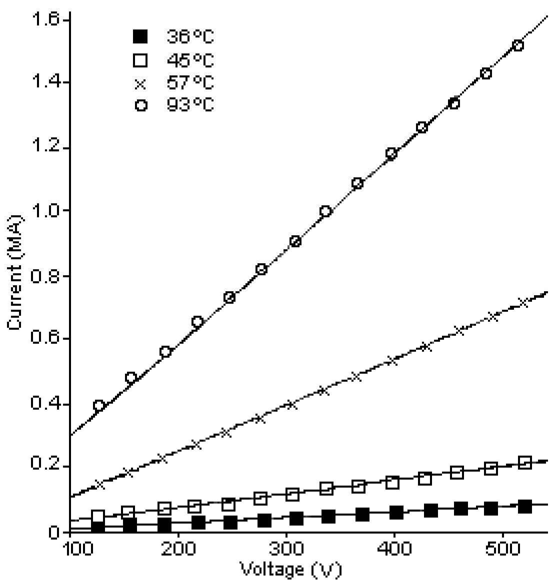
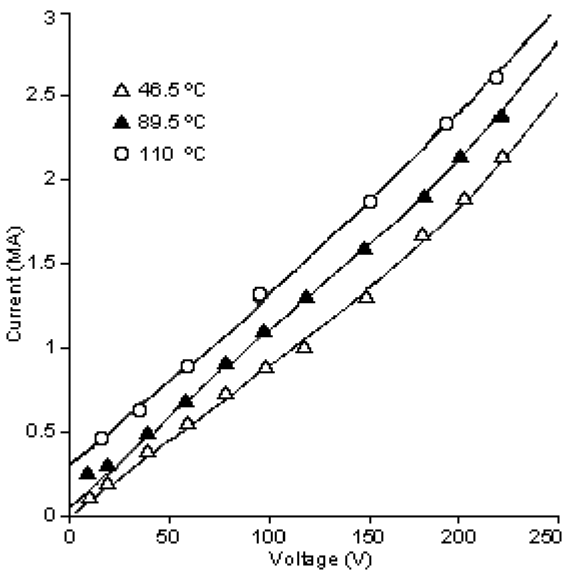


Figure 6: I-V plots for PbPMA.



Slopes of the plots between In1 vs 1000/T (k) at fixed voltages yield the activation energies for electrical excitation (Figure 4). CoPMA has different trapping levels which are progressively filled with the increase in temperature and voltage so different values of activation energies were obtained. These are in the range 0.102 to 0.162 ev.

The current voltage relationship for NIPMA at various temperatures is presented in Figure 5. An Ohmic conduction mechanism is operative at higher temperatures. As the temperature decreases the current values decrease and become independent of the voltage. The material thus acts as an insulator at room temperature. There is strong temperature dependence of current down to 318K, below which it becomes independent of temperature. This suggests that Schottky emission (10) is the dominant electron transport mechanism above 318K. The Schottky emission first observed by Emtage and Tantraporn (10) corresponds to the thermal excitation of electrons over metal-insulator/semiconductor interface barrier with the added effect that the applied field reduces the height of the barrier. The activation energy at low temperatures is approximately 0.8 ev. whereas, at high temperatures it is in the range of 0.21 to 0.27 ev.

The I-V plots for PbPMA presented in Figure 6 suggest that conduction increases with the rise in temperature. The deviation from Ohmic character at lower temperatures can be attributed to the fact that at lower temperatures electrons undergo small phase transitions. At high voltages the exponential rise is indicative of the Schottky of Poole-Frenkel conduction mechanisms. The activation energies at different temperatures range from 0.30 to 0.35 ev.

In order to sum up the above discussion it can be concluded that ;

These polymeric salts are semi conducting in nature as their conductivity rises with increase in temperature whereas, PMAA is an insulator. Hence the incorporation of metal atom in the pendant group of the parent polymer induces conducting properties. The conduction in these polymers is mainly electronic in nature as indicated by the low activation energy values.

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