Conductivity and DSC studies of poly(ethylene glycol) and its salt complexes

M V Murugendrappa, Syed Khasim & M V N Ambika Prasad
Department of Physics, Gulbarga University, Gulbarga 585 106, India

Received 25 February 2000; accepted 27 September 2000

The temperature response of conductivity of poly(ethylene glycol) (PEG) and its salt complexes like KCl, KBr and KI has been studied in the temperature range 299 to 331 K. Doping of PEG with KCl and KBr increased the conductivity by about 2.5 times for KCl and about 6.25 times for KBr, while doping with KI reduced the conductivity to about 0.05 times its pure component value. This may be due to the presence of dissolved salt in the solid, or alternatively may be due to the changes in the structure of PEG induced by the presence of salt. DSC studies on the samples were carried out wherein a beautiful peak was observed near the melting point. Analysis of DSC results confirms that the reaction is endothermic and the peak shifts towards higher value for different salts as compared to pure PEG.

PEGs are water soluble synthetic polymers having the general formula H-(O-CH₂CH₂)ₙ-OH. These materials have a wide range of applications, including use in pharmaceutical experiments, food additives and plasticizers¹. They are waxy materials available in different molecular weight grades and are commercially known as carbowax². The commercially available poly(ethylene glycol) [PEG-4000] has been used here and doped with KCl, KBr and KI. The conductivity studies of pure PEG and the effect of conductivity on its salt complexes have been studied. DSC studies are also carried out for all the samples.

Theoretical

In the characterization of electrical properties of a solid electrolyte, the most basic and useful information is the total conductivity and its fraction that is attributable to each charge carrier. There is a broad class of materials in which both ions and electrons are mobile. In the electrolyte materials with which we are now dealing, conductivity occurs by the migration of ions. The measurement of ionic conductivity or ion transport as it is often called, is non-trivial because of electrode-electrolyte interface³. In general, it is much more difficult to establish a low-resistance interface for ion flow than for electron flow.

Electrical conductivity may occur through the movement of electrons or ions. The conductivity (σ) of a polymer electrolyte is given by:

$$\sigma = n q \mu$$

where ‘n’ is number of ionic carriers per unit volume, ‘q’ is the charge of the carriers and ‘μ’ is the carrier mobility. The later parameter characterizes the ease with which the charged species will move under the influence of the applied electrical field.

In most cases of the amorphous polymer electrolytes, the conductivity variation as a function of temperature follows the following relationship³:

$$\sigma = \sigma_0 e^{-E_a / (k [T-T_o])}$$

where ‘σ₀’ is pre exponential factor, ‘Eₐ’ is activation energy and ‘Tₐ’ is the equilibrium glass transition temperature.

Among the different types of differential thermal techniques employed to characterize various physical and chemical changes taking place under isothermal or non-isothermal conditions, DSC is recognized as the technique of paramount importance⁴⁵. It involves the direct measurement of heat either liberated (exothermic) or consumed (endothermic) during a process. DSC is a technique in which the heat flow rate (power) to the sample is monitored against time or temperature, while the temperature of the sample is programmed in a specified atmosphere.

Experimental procedure

Known amount of PEG-4000 is taken in a crucible and heated on a water bath at about 60°C throughout the process, ensuring that the temperature is always less than the temperature of the decomposition of the polymer. When the sample gets melted, the known
amount dopant is added to it. For homogenous mixing, the stirring is done constantly by a mechanical stirrer. The sample is heated until it forms a homogenous solution. After the formation of the homogenous solution, it is poured on a watch glass and allowed to cool slowly, whereby a wax like solid is formed. We have doped KCl, KBr and KI to pure PEG up to 25%.

First, the sample is cut into regular shape and polished, and its dimensions measured. The crystal holder assembly is provided with steel electrodes each having diameter 1.0 cm. The test specimens used for the determination of resistance are in the form of rectangle or square. The specimens are coated with conducting silver for good electrical contact and are clamped firmly between the electrodes. This arrangement is found to provide good ohmic contact between the sample and electrodes in the conductivity cell and the dc conductivity is measured in the temperature range of 299-331 K.

The electrical conductivity is obtained by the standard dc conductivity technique by measuring resistance with the help of Keithley Solid state Electrometer (model 610 °C). The samples are heated slowly so as to avoid any thermal strains or shocks. The temperature is measured with a pre-calibrated Cr­Al thermocouple. The output of thermocouple is fed to a digital panel meter. The accuracy in the measurement of temperature is about ±0.5°C.

The DSC studies have been carried in the temperature range 303-343 K using T.A. instrument model-DSC 2010.

**Results and Discussion**

Fig. 1 shows the variation in electrical conductivity of pure PEG and its different salt complexes in the temperature range of 299-331 K while Table 1 shows the results at 299 and 331 K for PEG and its salt complexes. The temperature dependence of conductivity of the polymer salt complexes follows many patterns as discussed by Ratner and his co-workers (1987). From the conductivity-temperature plot (Fig. 1), it is observed that: (i) the conductivity increases with the increase of temperature in pure PEG and also in its salt complexes; and (ii) the conductivity-temperature plots follow the Arrhenius behaviour throughout.

In the above studies, the doping of PEG with KCl and KBr increases the conductivity about 2.5 times for KCl and about 6.25 times for KBr, while doping with KI reduces the conductivity to about 0.05 times its pure component value. The addition of salts progressively increases the amorphous phase in pure PEG. The increase of conductivity in case of PEG doped with KCl and KBr is due to faster internal modes in polymer chains in which bond rotations produce segmental motion. This, in turn, favours the hopping inter chain and inter chain movements and the conductivity of polymer salts becomes appreciable.

It is expected that the doping of salt enhances the conductivity of polymer salt complexes than the pure sample, because of the relationship between the chain motions of the polymer host and the diffusive or conductive mode of the ions. In a macromolecule, the size and spatial distribution of large molecules, which are in non-conducting crystalline phases, their conductivity is affected. In addition to the phase changes, the transformations requiring the redistribution of salts between phases are common.
and often take place over a long time scale affecting the relaxation time of the polymer and thereby affecting the conductivity. The increase in conductivity also depends upon the nature and the percentage of salt doped.

In spite of all the above factors, the conductivity in case of PEG doped with KI decreases by about 0.05 times when compared to pure sample. This is not clearly understood, but one may expect that the decrease in conductivity may be due to the high electron affinity of KI.

The activation energies of PEG and its salt complexes are determined from Fig. 1. The value of activation energies for pure PEG is found to be $0.2734 \times 10^{-6}$ eV, whereas for PEG doped with KCl, it is $0.2474 \times 10^{-6}$ eV; for PEG doped with KBr, it is $0.2439 \times 10^{-6}$ eV; and for PEG doped with KI, it is $0.2971 \times 10^{-6}$ eV. Thus, these activation energy values confirm that the conductivity increases for PEG doped with KCl and KBr whereas the conductivity decreases for PEG doped with KI.

Fig. 2 shows the DSC results of pure PEG and its salt complexes in the temperature range 303-343 K. In the DSC plots, there are two transition peaks between 60°C and 65°C, the larger one confirms the melting point of the sample and the smaller one is due to the presence of small amount of impurities in the sample. Table 2 shows the DSC results for PEG and its salt complexes. Analysis of DSC results confirms that the reaction is endothermic and the melting peak shifts towards the higher value for different salt complexes as compared to PEG.

**Conclusion**

The temperature response of conductivity may be employed to study the effect of doping on PEG, thereby giving information on the ionic transport of salt complexes in general and on the structure of these complexes in particular.

**References**