ORIGINAL RESEARCH PAPER

PHYSICS

INFLUENCE OF GAMMA IRRADIATION EFFECTS ON ELECTROCHEMICAL PROPERTIES OF POLYMER

KEY WORDS: Gamma irradiation; polymer electrolyte; ion conductivity

Pradyot Nanda

Physics Department, Dinabandhu Andrews College, Garia, Kolkata, West Bengal, India

ABSTRACT

The present study the thermal transitions and different phases of the polymer and changes in microstructure and resulting changes in the properties of PEO(1-x)-NH4ClO4(x) samples where x = 0.16,0.20,0.24,0.26 when irradiated with gamma doses varying up to 60 kGy. The ion conductivity shows a strong increase for an irradiation of 35kGy. Firstly-gamma radiation produces changes in microstructure and molecular weight of the system leading to dynamical disorder due to segmental motion of the polymer chains. The effect of gamma irradiation on polymers is mainly cross-linking and scission of the polymer chains. The present results, showing an exponential decrease in crystallinity with irradiation dose, is in conformity with earlier literature where cross-linking is held responsible for reduction in crystallinity.

1. INTRODUCTION

The ion conductivity of solid polymer electrolytes (SPE) can be improved on irradiation and the changes induced are permanent. The process is complex and depending on the dose, ambient conditions and other factors, there may be an increase or decrease in conductivity. Irradiation by gamma rays, electron beams or heavy ions leads to cross-linking and/or scission of the polymer chains that changes the molecular weight distribution and other details of molecular structure of the host polymer, which in turn affects the electrical and mechanical properties of the system [1,2]. I report the ion-conductivity results for PEO(1-x)-NH_4ClO_4(x) on gamma irradiation, in an attempt to identify the optimum salt concentration x and irradiation dose D where conductivity enhancement is maximum. Earlier work on the same material with x=0.12 did not show significant enhancement [3], while for x = 0.18, there was an enhancement by one order of magnitude for a dose of 35 kGy [7-9]. Impedance measurements reported in [7- 9]were done in the cooling cycle since cooling cycle measurements ensure better contact of the sample with the electrode and more reliable results. However, one cannot be sure if the initial heating has changed the sample characteristics. The impedance measurements reported in this tropic are done during heating. This may introduce some fluctuations in results at the cost of preserving the microstructure of the sample [4- 6]. Irradiation of polymers produces changes in microstructure and molecular weight [1] through cross-linking or scission of macromolecular chains. This may change the crystallinity and melting temperature as well as mechanical properties. Polymers complexed with a suitable salt are versatile solid electrolytes [2-5] due ease of preparation in different shapes and fairly good conductivity at ambient temperatures. The properties of the polymer electrolytes depend on the crystallinity and free volume available for ion motion, among other factors. So a study of the effect of irradiation on solid polymer electrolytes (SPE) is important, especially since equipment utilizing these may be subjected to radiation in reactors or spacecraft [5,6]. The present paper reports impedance measurements were done on a series of samples of PEO-NH_4ClO_4 irradiated by gamma rays with doses varying from 10 to 60 kGy.

Here, I show that conductivity in samples with a wide range of concentration (x = 0.16, 0.20, 0.24 and 0.26) to supplement the previous results. I find out that a dose of 30 kGy produces a enhancement of conductivity for x=0.16 and 0.20. The conductivity enhancement is strikingly large, by two orders of magnitude, for sample with x = 0.16, which is not seen in samples with higher salt concentration. For samples with x=0.24 and x=0.26, the conductivity increases appreciably with irradiation.

Another interesting observation is the presence of inductive behaviour in samples with higher x. While such effects, sometimes observed at low frequencies, are usually attributed to the geometry of the setup, in the present study, I find out this at high frequencies. This may be an indication of peculiarities in the molecular structure.

2 EXPERIMENTAL

2.1 Sample preparation

Poly-(ethylene oxide) from B.D.H., England (Mol wt. $6x10^5$), methanol (99.9 % pure) and ammonium perchlorate (Fluka, 99.5%) have been used for sample preparation. The polymer films have been prepared by the solution casting technique, dissolving the solid components in methanol. Fraction x by weight of NH_4ClO_4 and (1-x) fraction of PEO were together dissolved in methanol. The suspension was stirred for 14-16 hours at room temperature (~305 K). Films were cast on a Petri dish, dried in air for 4-5 days and then vacuum dried for 3-4 days. The average thickness of the films was about 250 μm. I thus prepared films each having total mass 2 gm and composition: PEO(1-x)-NH_4ClO_4(x), with x = 0.16, 0.20, 0.24, 0.26.

2.2 Gamma Irradiation

The samples were irradiated in a conventional gamma chamber, which uses a ^{60}Co source with a dose rate of 60 Gy/min or 6 Krad/min. I report results for samples with doses 10 to 60kGy for varying x and compare their properties.

2.6 Impedance Spectroscopy

Impedance spectroscopy has been carried out at IIT, Kharagpur on a Hioki LCR Hi Tester (model:3520) in the frequency range 1 to 10^5 Hz. The temperature range of measurement is 35°C to 55°C.

3 RESULTS

IS studies indicate remarkable effects of gamma irradiation on polymer electrolyte samples with x=0.16 , 0.20, 0.24 and 0.26.

3.4 Impedance Spectroscopy

Impedance spectroscopy results for different concentrations and gamma doses have been analyzed for the samples. A detailed study of the complete Cole-Cole plot reveals features which may give important information about the sample. The Cole-Cole plots at a specific radiation dose but at different temperatures for samples with x= 0.16, 0.20 and 0.24 are shown in fig. 1(a)-1(e). The real part of admittance versus frequency plots for x=0.16 and 0.24 are shown in fig. 2(a) – 2(b).

The DC conductivity can be obtained from a Cole-Cole plot by locating the points on the real Z axis. A plot of the dc conductivity vs. gamma radiation dose for the different samples at 35°C is shown in fig.3. The samples with both x=0.16 and x=0.20 show an increase in conductivity at 30kGy irradiation and a subsequent drop at 40 kGy. However, samples with x=0.24 shows a maximum conductivity at around 20 kGy dose with a fall at higher doses while samples with x=0.26 shows a steady rise in conductivity with increase in radiation dose. A close comparison of the dc conductivity plots for x=0.16, 0.20, 0.24

with x= 0.26 reveals that there can be an enhancement in conductivity at around 30 kGy dose for x=0.26 which has not been experimentally detected. Samples with x =0.20, 0.24 and 0.26 salt concentrations shows a slight decrease in conductivity at 10 kGy followed by appreciable increase in conductivity at higher doses. These results are consistent with the earlier study on samples with x=0.18, where similar behaviour was observed [7]. However, for x =0.18, the IS set up was different and the measurements were done on the cooling cycle, so a quantitative comparison of conductivity results for x=0.18 with those for x=0.16, 0.20, 0.24 and 0.26 will not be meaningful.

The significant new result is that for x = 0.16, the enhancement in conductivity is much higher compared to other cases. In the Cole Cole plot the low frequency regime is attributed to impedance of the electrodes with two semicircles representing the sample impedance. These two semicircles arise due to the presence of two different conducting phases or due to existence of a phase boundary between the amorphous crystalline phases in the samples.

Equivalent circuits consisting of combination of resistors, inductors and capacitors can be employed with suitably chosen parameters to give a best fit with the Cole-Cole plots and real part of admittance vs. frequency plots and explain the presence of inductive loops at high frequency in samples [8]. While I cannot rule out the possibility of the inductive feature being due to peculiarities of the setup, or to transient effects [9,10] it may possibly reflect the peculiarities in the salt-polymer microstructure with helically coiled polymer molecules [11]. The helical structure of PEO chains is well established and it is known that the ions of the electrolyte occupy positions within the polymer coil structures [12,13]. Spirally coiled or zigzag polymer molecules [14,15] may affect the path of charge carriers and induce a winding motion.

3.4.1 Temperature variation of conductivity

The temperature variation of conductivity for sample with x=0.20 for different radiation doses is shown in Log (σ) vs. 1/T plots in figure 4. The plot is almost linear for the unirradiated sample, but becomes rather non-linear on irradiation. The average slope for dose (D) = 30kGy is less than that of the unirradiated sample, indicating that the activation energy is lower in this case.

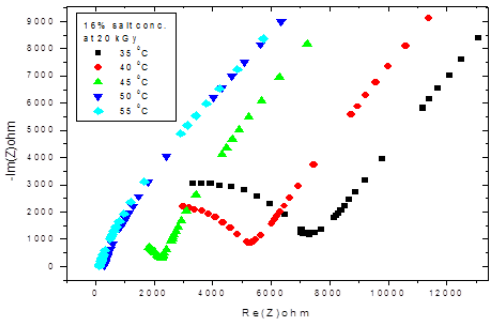

Figure 1(a): Zoomed high frequency regime of the Cole-Cole plot for the sample with x=0.16 irradiated with 20 kGy gamma dose at different temperature.

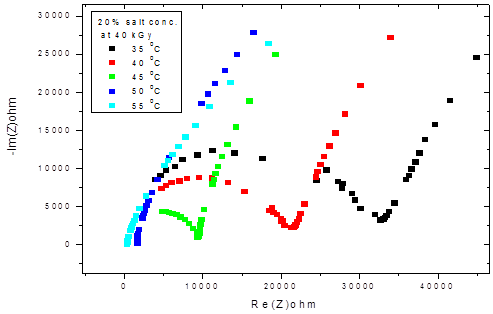

Figure 1(b): Zoomed high frequency regime of the Cole-Cole irradiated with 10 kGy gamma at different temperatures.

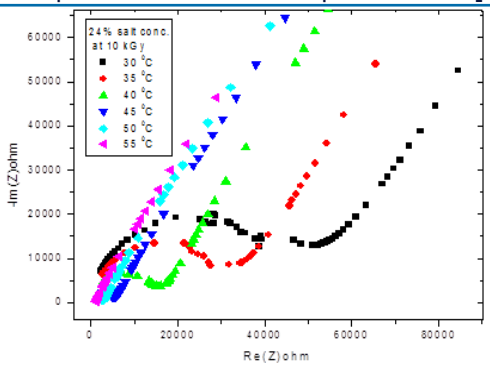

Figure 1(c): Cole Cole plot for the sample with x=0.24 plot for the sample with x=0.20 irradiated with 40 kGy gamma dose at different temperatures.

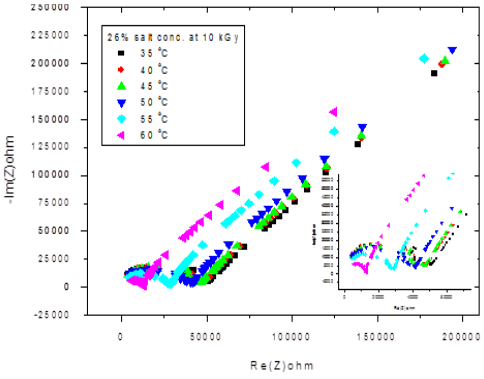

Figure 1(d): Cole Cole plot for the sample with x=0.26 irradiated with 10 kGy gamma at different temperatures. Inset shows high frequency region of the graph.

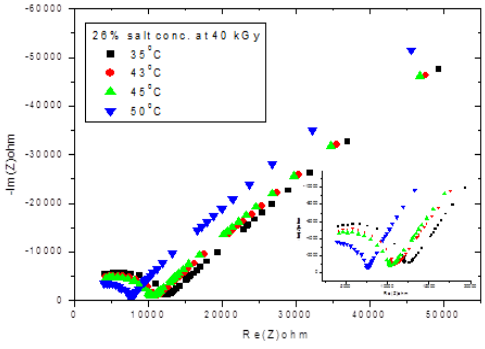

Figure 1(e): Cole Cole plot for the sample with x=0.26 irradiated with 40 kGy gamma at different temperatures. Inset shows high frequency region of the graph.

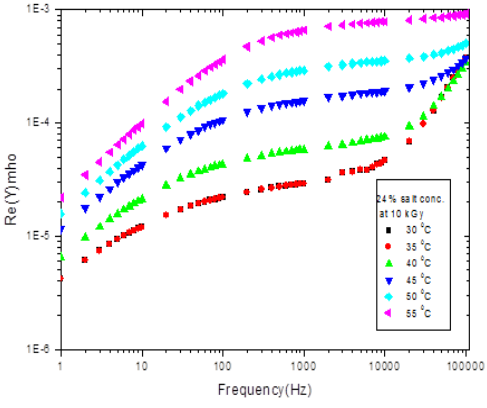

Figure 2(a): Double logarithmic plot of real part of admittance vs. frequency for the sample with x=0.24 irradiated with 10 kGy, at different temperatures.

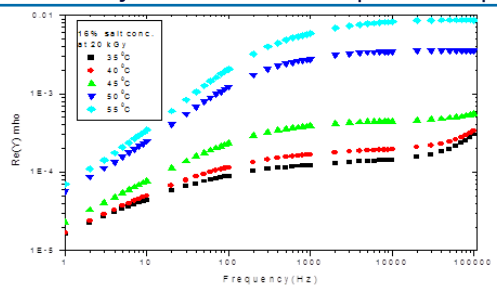

Figure 2(b): Double logarithmic plot of real part of admittance vs. frequency for the sample with x=0.16 irradiated with 20 kGy at different temperatures.

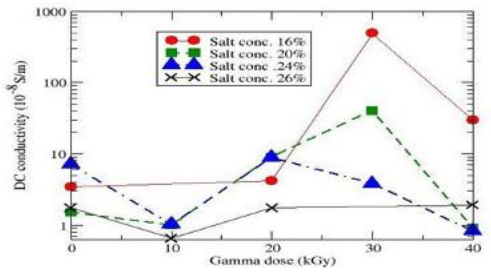

Figure 3: The DC conductivity (on logarithmic scale) versus radiation dose for samples with x=0.16, 0.20, 0.24 and 0.26 at 35 °C.

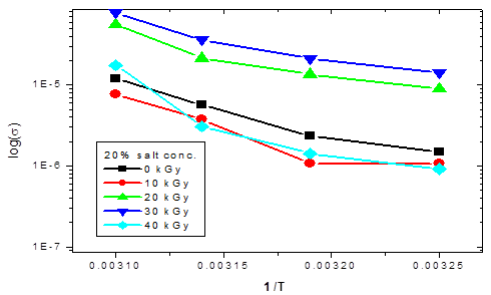

Figure 4: Log(σ) vs. 1/T for samples with x=0.20 irradiated with different gamma doses

DISCUSSION

The present study shows that ion-conductivity is highly sensitive to both salt concentration x and radiation dose D. Up to a particular value of x, conductivity increases due to increase in charge carrier concentration but falls subsequently for higher x. This is mainly due to increase in crystallinity or ion-association effects [16,17]. The most striking result obtained in this study is the large enhancement in ion-conductivity (σ) obtained for the x=0.16 sample at 30 kGy. This enhancement by two orders of magnitude is much larger than for other concentrations. It will be useful to study different concentrations and irradiation doses at closer intervals, in order to identify the regime where enhancement is most pronounced. However earlier for x = 0.12, σ was found to be very low and irradiation did not produce significant improvement [3]. The explanation for the initial increase and subsequent decrease in conductivity on irradiation is an interesting question. The effect of gamma irradiation on polymers is primarily cross-linking and/or scission of the macromolecular chains [18]. These two processes take place simultaneously although usually one dominates over the other depending on several factors. In general, scission increases flexibility and segmental motion of the chains, leading to an increase in conductivity. However, scission may also increase crystallinity since smaller chains align and form ordered arrays more easily. This again can decrease conductivity, since it is well established that crystallinity hinders ion motion [16-20]. The effect of cross-linking may also work both ways. Up to a point cross-linking results in reduced crystallinity, hence enhanced conductivity, but ultimately a rigid three-dimensional network, allowing very little ion motion, is produced by increased cross linking.

A comparison of this study with the one made by Damle et al. have found an enhancement of two orders of magnitude in conductivity by irradiation, however in their case the material is PEG-NH_4I and irradiation is done by electron beam only for a dose of 10 kGy. So variation with dose cannot be ascertained [19].

Another point regarding our results should be mentioned. There is some controversy regarding whether IS readings should be taken during heating the sample or during cooling. Heating cycle results may be unreliable due to poor contact between the sample and electrode, on the other hand, if readings are taken during cooling, one is never sure if the initial heating has produced irreversible changes in the morphology and hence conductivity. The present set of results recorded during heating, do not quantitatively match the earlier results for x=0.18 [7], but the qualitative behaviour with the conductivity peaking at around D=30 kGy, is exactly similar.

CONCLUSIONS

To conclude, firstly-gamma radiation produces changes in microstructure and molecular weight of the system leading to dynamical disorder due to segmental motion of the polymer chains. The ion conductivity of solid polymer electrolytes (SPE) improves on irradiation. In most of the samples the d.c. conductivity increased to a maximum at around 30 – 35 kGy. The ion conductivity is highly sensitive to both salt concentration and radiation dose. The largest enhancement in ion-conductivity, almost by two orders of magnitude is for x=0.16, although exact reasons for such large increase in conductivity is not understood. Impedance Spectroscopic studies indicate presence of inductive behavior in samples with higher x probably due to the peculiarity in polymer-salt microstructure. PEO molecules being helically coiled, the charge carriers may have a winding motion which shows up as induction. The effect of gamma irradiation on polymers is mainly cross-linking and scission of the polymer chains. Although both the processes occur simultaneously, usually one dominates over the other depending on several factors. Scission increases segmental motion of the polymer chains, leading to an increase in conductivity. However, sometimes due to alignment of smaller chains, crystallinity increases leading to decrease in conductivity. Although crosslinking leads to greater amorphicity, hence enhanced conductivity, but ultimately a rigid three-dimensional network is formed due to heavy crosslinking that significantly lowers conductivity.

It is seen that the conductivity for sample with 16% salt concentration increases by two orders of magnitude at a radiation dose of 30kGy and this enhancement of conductivity is maximum for this sample compared to x= 0.20, 0.24, 0.26. Hence investigation with salt concentration x< 0.16 can be a very relevant study. Detailed investigation regarding conductivity of sample with salt concentration from 12% to less than 16% can throw light on the changes in the microstructure of the sample as well as indicate the role of scission and cross-linking in such changes.

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