Ionic conductivity of PEO-NH$_4$ClO$_4$ films by admittance spectroscopy: Correlation with crystallinity and morphology

Aninda Jiban Bhattacharyya,* T. R. Middya, and S. Tarafdar

Department of Physics, Condensed Matter Physics Research Centre, Jadavpur University, Calcutta 700032, India

(Received 18 November 1998; revised manuscript received 29 January 1999)

In this paper we present a study of ionic conductivity versus salt fraction for PEO-NH$_4$ClO$_4$ films. Films with salt concentration x in the range $0-0.35$ (x is the weight fraction of the salt) were prepared for the study. X-ray diffraction and differential scanning calorimetry were done to detect the different species present and to estimate the crystallinity of the films. The films have a wide variety of structures and exhibit a transformation from fractal to nonfractal morphology as x is increased. We attempt a correlation of ionic conductivity with crystallinity and morphology of films with varying x and find that the fractal to compact crossover region has the highest ionic conductivity. [S0163-1829(99)12825-X]

I. INTRODUCTION

Solvent free polymer electrolytes are a class of superionic solids which are formed by dissolving an ionic salt in a high molecular weight ($\sim 10^6$) polymer.[1–3] These materials have tremendous potential applications as solid electrolytes in electrochemical devices.[1–3] Research interest on such materials began with the pioneering studies based on alkali metal salt complexes with polyethylene oxide (PEO) by Wright[4] and Armand.[5] Since then a wide variety of solvent free polymer electrolytes have been prepared. Apart from the use of different polymers and salts, solvent free polymer electrolytes have also been prepared by varying polymer architecture[1] (e.g., from linear polymer host to branched or network polymer host).

The polymer itself is an insulator, but when a suitable salt is complexed with it, the salt may supply ions to act as charge carriers. The polymer-salt complex in this case acts as a good ionic conductor with the polymer host providing easy paths for diffusion of the ions.

Many polymer electrolytes are biphasic in nature,[1–3] i.e., both amorphous and crystalline phases are simultaneously present in the same sample. This influences physical properties like ionic conductivity, crystallinity, etc. of the polymer electrolyte. The study of variation in ionic conductivity (σ) with salt fraction (x) is an interesting but formidable problem for both experimental and theoretical research.

In a previous work[6] we showed that the morphology of PEO-NH$_4$ClO$_4$ films undergoes a drastic change, from tree-like aggregate structures in a featureless matrix to compact polygonal regions. In the present work we show that the crossover region has the highest ionic conductivity and correspondingly the lowest crystallinity.

We present a study of ionic conductivity versus salt fraction x of polyethylene oxide (PEO) films complexed with ammonium perchlorate (NH$_4$ClO$_4$). X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were done to detect the different species present in the films and to estimate the crystallinity of the films. The method of sample preparation is given in the next section, and experimental results on ionic conductivity, x-ray diffraction and differential scanning calorimetry are presented in Sec. III. The morphology variation with x for PEO-NH$_4$ClO$_4$ studied earlier[6] is discussed briefly in Sec. III D. In Sec. IV we try to correlate ionic conductivity to crystallinity and morphology, and in Sec. V we summarize our conclusions.

II. EXPERIMENTAL PROCEDURE

A. Preparation of the films

A detailed account of the preparation of the films has been discussed in Ref. 6. For this study, we prepared films of both pure PEO (BDH, England; M.W.=600000) and PEO complexed with ammonium perchlorate (Fluka, 99.5% pure), by solution casting technique with methanol (hplc grade) as the solvent. Films with a weight fraction $x=0-0.35$ of NH$_4$ClO$_4$ were prepared for the study. For each concentration three sets of samples were prepared for reproducibility. The thickness of a typical film was approximately 150 μm and the diameter was 7.5 cm.

B. Characterization methods

The conductance was measured from the admittance plots obtained using HP4274A LCR meter (100 Hz–100 KHz) between temperatures (35–62)°C. The films were held between spring-loaded brass electrodes and conductivity was measured in the cooling cycle. The heating cycle did not produce reproducible results presumably due to lack of good contact with the electrodes.

X-ray diffraction was done by using an x-ray diffractometer Philips PW 1730/10 with Traces v3.0 diffraction software. For differential scanning calorimetry (Perkin Elmer DSC 2) samples weighing approximately 5 mg were heated at a rate of 5 °C/min from 40–140 °C in Nitrogen gas flow. The melting enthalpy has been estimated by comparing the area under the melting curve of the samples with that of Indium ($\triangle H_m = 6.8$ cal/gm, $T_m = 156.60$ °C). For crystallinity estimation, the melting enthalpy for 100% crystalline PEO was taken to be 45 cal/gm.[7]

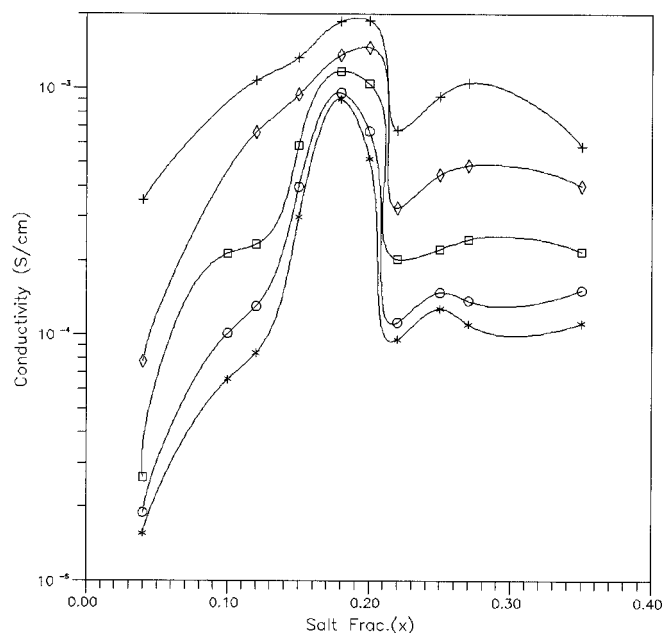FIG. 1. Plot of conductivity σ versus salt fraction x at (a) 35 °C ($\star$), (b) 40 °C ($\bigcirc$), (c) 47 °C ($\square$), (d) 55 °C ($\diamond$), and (e) 62 °C ($+$). The error bars are of the order of the symbol size.

III. EXPERIMENTAL RESULTS

A. Ionic conductivity measurement

The ionic transference number was estimated using Wagner's polarization method.[8] Our apparatus being manually controlled, the value cannot be determined very accurately but it is not less than 0.94. This suggests that the charge transport in PEO-NH$_4$ClO$_4$ system is principally ionic with negligible electronic conduction.

The ionic conductivity is estimated at different temperatures and salt fraction. Figure 1 shows variation of ionic conductivity (σ) with salt fraction (x) at temperatures 35 °C, 40 °C, 47 °C, 55 °C, and 62 °C, respectively. At all temperatures σ increases with x, with a maximum at $x \approx 0.18$.

In polymer electrolytes σ depends on both temperature and salt fraction. σ increases with temperature and usually the results of σ versus temperature can be fitted to the well known Arrhenius or VTF forms[1–3] depending on the host polymer. On the other hand, the variation of σ with x is nontrivial. In Ref. 2 it is proposed that the behavior can be approximated as parabolic. But experiments indicate that the behavior may be more complex in general.

In our study we see that as temperature is increased for a particular x, σ increases as expected. At the highest temperature studied 62 °C, the sample is above the melting temperature for PEO (58 °C). There is an enhancement of ionic conductivity from $\sim 10^{-4}$ S/cm at $x=0.04$ to $\sim 10^{-3}$ S/cm at $x=0.18$–0.20.

For samples at $x=0.10$ and $x=0.12$ diffusion limited aggregate[6] (DLA) patterns were obtained unlike the higher x samples which formed polygonal regions. To understand more fully the effect of morphology variation, regions with and without trees were cut out from the same sample and σ was measured in both cases. Figure 2 shows σ versus temperature for $x=0.10$ for regions with and without DLA growth. At temperatures below the melting point of the PEO,
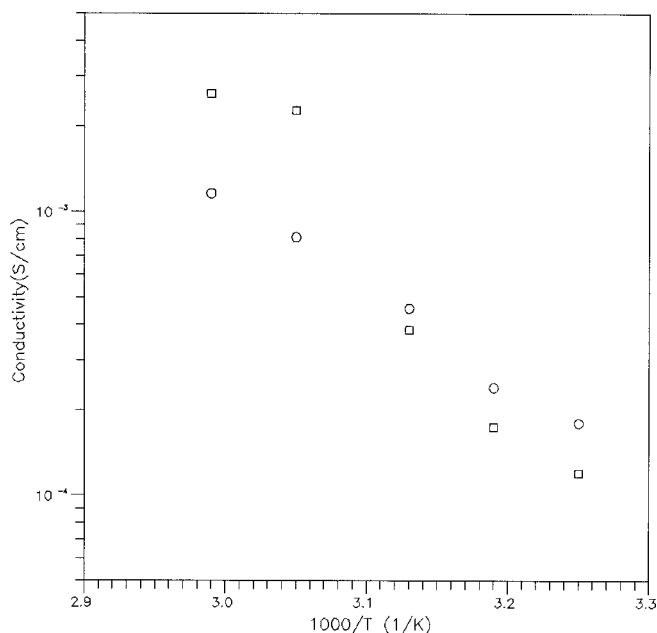

FIG. 2. Plot of conductivity σ versus temperature (T) at $x=0.10$ for two different regions of the same film. (a) Tree region ($\bigcirc$) and (b) no tree growth ($\square$).

σ for the region with DLA growth is slightly higher than for the region without any tree growth.

B. X-ray diffraction studies

Figure 3 shows the diffraction patterns for pure PEO ($x=0$), NH$_4$ClO$_4$($x=1$) and PEO complexed with NH$_4$ClO$_4$ for $x=0.04$, 0.10 (tree regions and no tree regions), 0.18, 0.20, and 0.35. The peaks corresponding to pure crystalline PEO at approximately $2\theta=19.3°$, $23.1°$, $23.5°$, $26.5°$, and $27.3°$ are present nearly in all samples but with varying intensities. The pure PEO peaks seem to be more intense for lower values of x ($x=0.04$). With increase in x ($x \geqslant 0.18$) lines corresponding to PEO-NH$_4$ClO$_4$ complex become dominant. Broad peaks obtained for $2\theta=13.8°$, $14.3°$, $17°$, $18.9°$, and $21.5°$ are attributed to the formation of a polymer salt complex in the intermediate range and signify that the samples are of low crystallinity.

For samples containing DLA growth ($x=0.10$) we show the XRD patterns for two regions one with tree growth [Fig. 3(c)] and the other without [Fig. 3(d)]. Figure 3(d) showed predominantly lines corresponding to crystalline phase of pure PEO at $2\theta=19.4°$, $22.6°$, $23.9°$. It also showed lines of polymer salt complex (less intense compared to PEO) at $2\theta=14°$ and $17°$. But the spectrum in Fig. 3(c) was quite different. In this case pure PEO lines were stunted and the lines at $2\theta=14°$ and $17°$ were highly intense (even more than that of pure PEO lines for the region with no tree growth). This suggests that the region with tree growth contains the PEO-salt complex in crystalline form.

From optical microscopy and variable temperature polarizing microscopy (VTPM) it was confirmed that for $x \geqslant 0.30$ all of the salt does not form complex and the excess remains as separate crystals in the film. A highly intense peak corresponding to the complex ($2\theta=17°$) was obtained here. Probably the crystallinity of the complex has increased
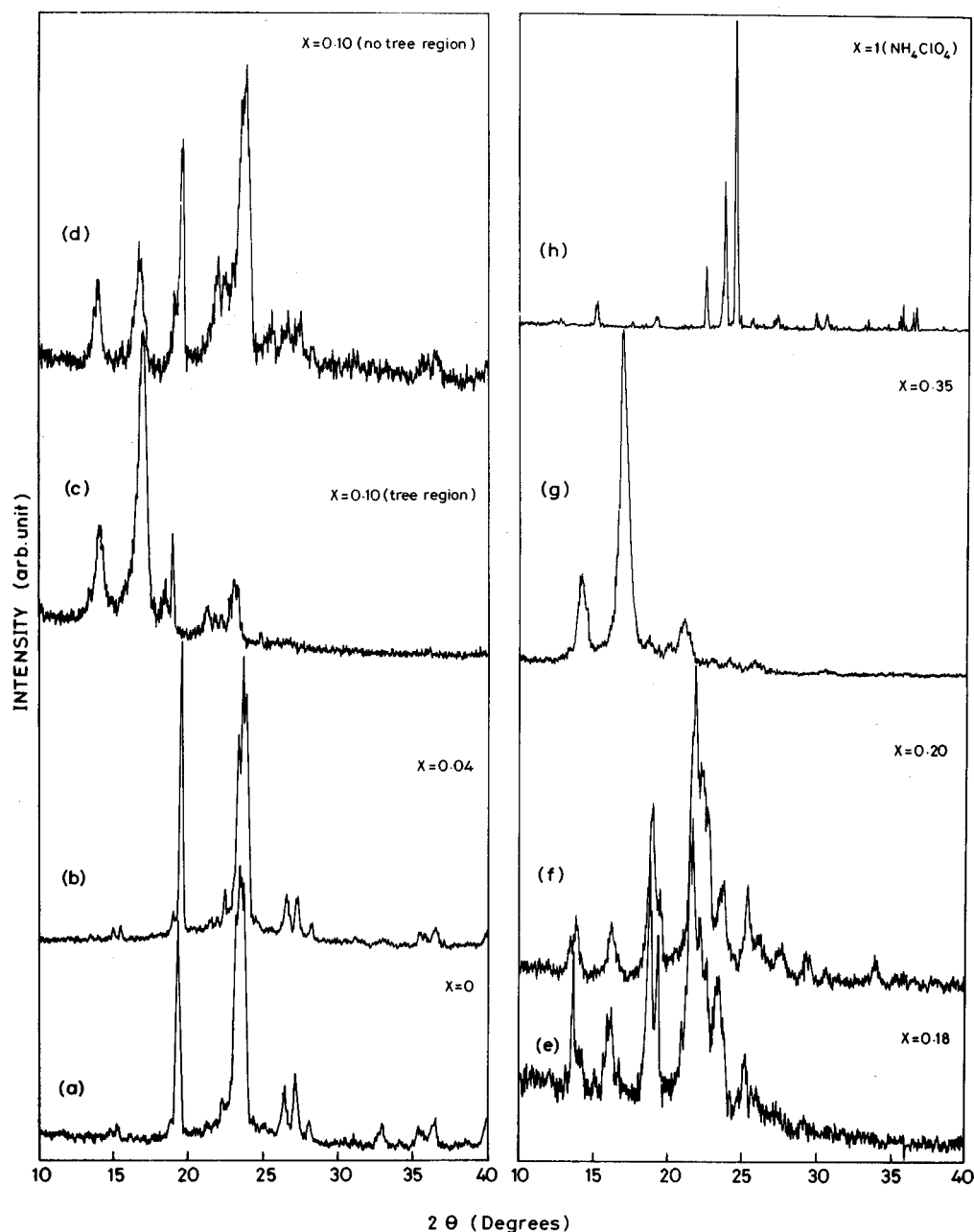
FIG. 3. X-ray diffraction patterns for (a) pure PEO, (b) $x = 0.04$, (c) $x = 0.10$ (tree growth), (d) $x = 0.10$ (no tree), (e) $x = 0.18$, (f) $x = 0.20$, (g) $x = 0.35$, and (h) pure NH_4ClO_4.

compared to the intermediate range. No lines for pure NH_4ClO_4 are however observed. It is possible that the portion of the film studied did not contain any crystallite of excess salt.

C. Differential scanning calorimetry

Figure 4 shows the melting endotherm for pure PEO and PEO–salt, complexes for $x = 0.04$, 0.10, 0.18, 0.20, 0.22, and 0.35. Crystallinity variation with x as inferred from DSC results is shown in Fig. 4.

For DSC study of the films with DLA growth, it is seen from Fig. 4(c) that the sample with no tree growth was slightly less crystalline than that with tree growth [Fig. 4(d)]. Table I shows the melting and crystallinity at different x.

D. Study of morphology by polarizing microscopy and photographs

We discuss here briefly the various types of morphology obtained for films of PEO complexed with NH_4ClO_4. The transition from fractal to nonfractal structures obtained by varying weight fraction of NH_4ClO_4 ($x = 0 - 0.35$) has been discussed in detail in Bhattacharyya et al.[6] The detailed structure of the films were observed through a polarizing microscope (Leitz Ortholux 2) and by photography.

The morphology obtained can be strictly divided into three broad classes: Low x regime ($0 \leqslant x \leqslant 0.15$), intermediate x regime ($0.18 \leqslant x \leqslant 0.27$), and high x regime. Table II summarizes the various characteristics of the films obtained for varying x.

TABLE I. Melting enthalpy and crystallinity at different salt fractions.

Salt fraction (x)	Melting enthalpy (cal/gm)	Crystallinity %
0	43.50	96.7
0.04	32.00	71.1
0.10 (no tree growth)	10.30	22.9
0.10 (with tree growth)	12.06	26.8
0.18	1.61	3.6
0.20	12.36	41.8
0.22	17.88	60.47

1. Low x regime

Spherulites of pure PEO are formed[6] in the low x regime ($x=0.04, 0.08$). They are small, irregular, and somewhat rounded. At $x=0.10$ and 0.12 fractal DLA patterns are obtained as shown in Figs. 5(a) and 5(b). The Hausdorff dimension (by box counting method) is ~ 1.8 [Fig. 5(a)] for length scales (0.4–11.4) mm which is typical of DLA. Increase in x results in more nucleating islands and smaller sized trees [Fig. 5(b) and Table II], distributed densely.

For small length scales of the order of the thickness of a branch of the trees, the trees are no more mass fractal but surface fractal, dimension of the boundary is ~ 1.5 (estimated by the divider step method).

On slightly increasing x from 0.15 to 0.18, there is a drastic change in morphology.

2. Intermediate x regime

In the intermediate regime ($0.18 \leq x \leq 0.27$) the film is marked by large compact polygonal spherulites (Fig. 6). Under the cross polarizer, each polygonal spherulite has a Maltese cross pattern[9] in the center and a directional texture is clearly visible at the boundary between adjacent polygons. The polygon size increases with x, and then grows smaller (maximum linear size is seen at $x=0.20$).

3. Higher x regime

For salt fractions higher than $x=0.30$, excess salt remains uncomplexed and can be seen as separate crystals on the
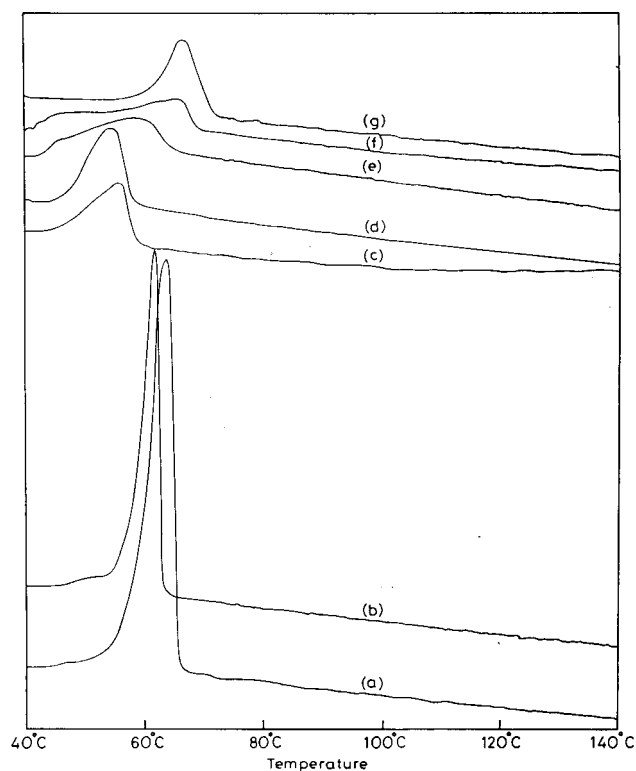

FIG. 4. Differential scanning calorimetry curves for (a) pure PEO, (b) $x=0.04$, (c) $x=0.10$ (no tree), (d) $x=0.10$ (tree growth), (e) $x=0.20$, (f) $x=0.22$, and (g) $x=0.35$.

film, with spherulites in the background.[6] This is also confirmed by variable temperature polarizing microscopy (VTPM) where at 68 °C only grains of salt remain and the other phases have melted.

IV. CORRELATION BETWEEN IONIC CONDUCTIVITY, CRYSTALLINITY, AND MORPHOLOGY

Let us now compare the information obtained from the different characterization techniques and see what useful insight can be gained from this study.

Figure 1 shows the measured σ versus x for different

TABLE II. Variation of morphology with different salt fraction.

Concn. of NH_4ClO_4 (x)	Morphology	Average spherulite/tree size
0 (Pure PEO)	Small spherulites	360 μm
0.04	"	200 μm
0.08	"	150 μm
0.10	Large trees+microscopic spherulites	1.3 cm
0.12	"	0.214 cm
0.15	"	0.15 cm
0.18	Large polygonal spherulites	0.242 cm
0.20	Largest polygonal spherulites	2.0 cm
0.22	Polygonal spherulites	1.4 cm
0.25	"	0.9 cm
0.27	Small sized spherulites	0.7 cm
0.30	Small amounts of salts	
0.32	remain unreacted, polygonal spherulites	250–350 μm
0.35	in the background	

FIG. 6. Photograph PEO-NH$_4$ClO$_4$ at $x=0.22$ showing polygonal spherulites (avg. size ∼1.4 cm) (scale = 1 cm; magnification: ×2.2).

Shriver[1] and Vincent[2] by the fact that the salt acts as a cross linker between the polymer chains. We suggest an explanation based on the morphology variation with x.

The crystallinity versus x and σ versus x curves are shown simultaneously in Fig. 7, and Fig. 8 shows spherulite size versus x together with σ versus x. The crystallinity shows a dip as x increases, and the minimum coincides clearly with the maximum in σ. This shows that the amorphous regions allow much higher mobility for the charge carriers. Figure 7 and Table II show that the maximum in σ corresponds to the crossover region for DLA (i.e., fractal patterns) to compact polygonal spherulites. The sharp fall in σ occurs in the region where the largest polygons are formed.

According to XRD and DSC results, the pure PEO is highly crystalline ∼90%. For very low x PEO-NH$_4$ClO$_4$ complexes form (as shown by the new XRD peaks) but the crystallites are very sparsely distributed in the PEO matrix.

FIG. 5. Photograph of DLA pattern obtained for PEO-NH$_4$ClO$_4$ at $x=0.10$ (scale = 1 cm; magnification: ×4.5). (b) As crossover region is approached trees become smaller and more closely spaced as seen in the photograph for $x=0.12$ (scale=1 cm; magnification: ×3.3).

temperatures. Initially, there is a rise in σ as x increases from zero. Pure PEO has no charge carriers, increase in x increases the concentration of carriers, so σ increases, as expected. After reaching a peak at $x\sim0.18$, σ falls sharply around $x=0.22$. Interpretation of this fall is not so straightforward, as x is still increasing. This has been explained by Ratner and
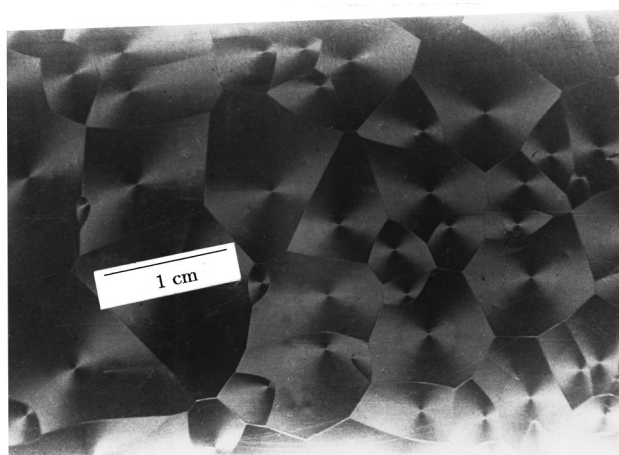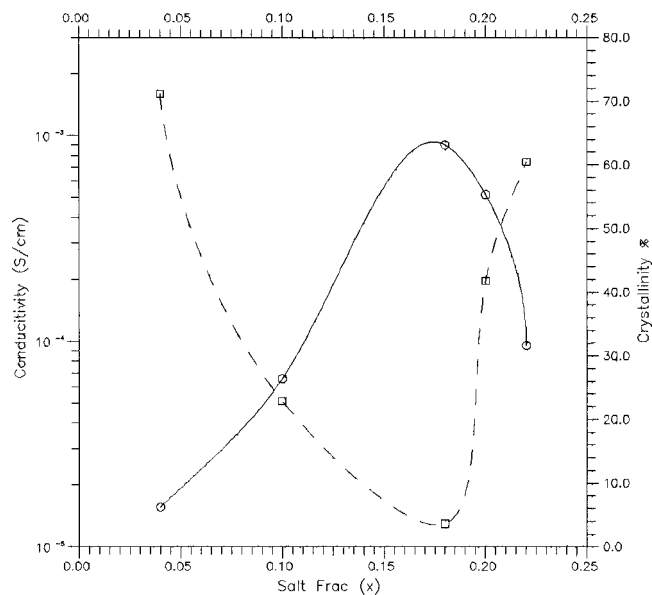

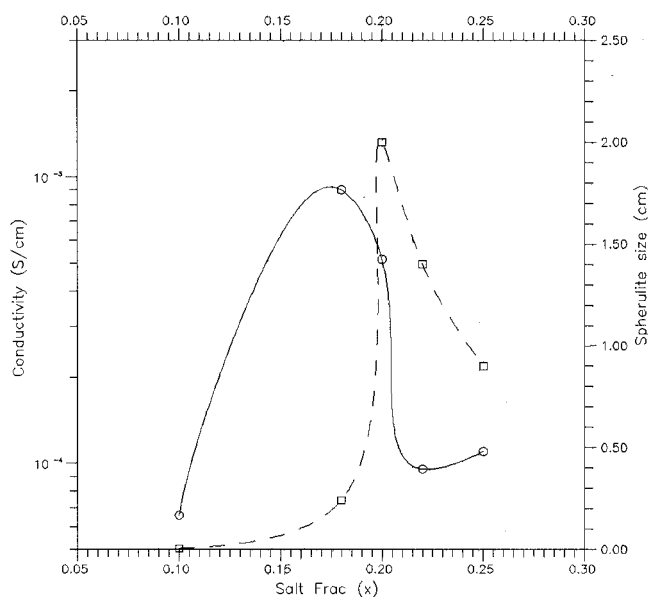FIG. 7. Plot of crystallinity versus x (□) and σ (at 35 °C) versus x(○).

FIG. 8. Plot of spherulite size versus x ($\square$) and σ (at 35 °C) versus x ($\bigcirc$). For $x < 0.18$, size of pure PEO spherulites are considered.

We suggest[6] that they perform a random walk through the still undried film and form the typical DLA type patterns with Hausdorff dimension ~1.8. The background of the trees is mostly pure PEO which is highly crystalline. So the overall crystallinity in this region is high.

With increasing x, more PEO-NH$_4$ClO$_4$ complex crystallites are formed and more nucleating centers develop, so densely distributed small trees are formed, rather than a few widely separated large trees. The regions in the interstices between the small DLA aggregates are likely to be the most amorphous. Such regions are most abundant in the crossover region ($x = 0.15$–0.18) where the tree growth is about to change to compact spherulites. This is corroborated by the DSC results for crystallinity. The measurements of σ for the sample at $x = 0.10$ shows higher σ, for the region with DLA. This agrees with our suggestion. The lower crystallinity for the sample with no DLA growth appears to contradict σ results. But the difference is very small. It must also be kept in mind that σ measurements are done on the cooling cycle, and the local morphology may change during measurement. So it may be misleading to attach too much importance to the results for ''with tree'' and ''without tree'' samples at same x.

For higher $x > 0.18$, the composition is such that most of the PEO goes into the complex phase. Regularly ordered circular spherulites grow and develop into polygons which are seen in the micrograph and crystallinity increases. In general, we may say that the initial rise in σ is due to increase in

concentration of charge carriers and the subsequent fall is due to a decrease in their mobility.

The polymer spherulites are, of course different from perfect crystalline materials, and always have some amorphous regions between the aligned polymer chains. So, σ does not drop to zero in the polygonal phase.

V. DISCUSSION AND CONCLUSION

In this work we explain the nonmonotonic variation of σ in PEO-NH$_4$ClO$_4$ through variation in morphology. It may be noted however that for MEEP-AgSO$_3$CF$_3$, Blonsky et al.[10] have found nonmonotonic behavior for σ versus x though the polymer is fully amorphous. This has been explained as being due to crosslinking at higher x. An earlier work by Lee and Crist[11] investigated a similar problem for PEO-NASCN films at different salt fraction and temperatures. They assumed conduction only through the amorphous phase and calculated the ionic conductivity variation using the WLF relation.

The PEO-NH$_4$ClO$_4$ system has been previously studied by Hashmi et al.,[12] so it is instructive to compare their results with ours. Hashmi et al.[12] did measurements in the cooling cycle at six different ratios of [EO]/NH$_4^+$ ([EO] is the monomer unit of the polymer) in the range 20:1 to 7:1. The results are more or less in agreement with ours. However they do not report occurrence of DLA structures for this system. We have covered a wider range of x values 66:1 ($x = 0.04$) to 5:1 ($x = 0.35$), with closely spaced observations, and correlated the observations with morphology and crystallinity variation.

In conclusion, we have presented a qualitative picture of the ionic conductivity variation of a typical polymer-salt system. We hope to explain our experimental results quantitatively through ongoing computer simulation studies. Some preliminary work has been reported.[13,14] We have also studied the effect of dynamic disorder due to movement of the polymer chain segments through computer simulations on a rearranging lattice in two dimensions.[14] This effect is to be incorporated into the study of temperature and x variation of the ionic conductivity.

*Electronic address: aninda@juphys.ernet.in

[1] M.A. Ratner and D.F. Shriver, Chem. Rev. **88**, 109 (1988).

[2] C.A. Vincent, Prog. Solid State Chem. **17**, 145 (1987).

[3] D. Baril, C. Michot, and M. Armand, Solid State Ionics **94**, 35 (1997).

[4] D.E. Fenton, J.M. Parker, and P.V. Wright, Polymer **14**, 589 (1973).

[5] M. Armand, J. M. Chabagno, and M. Duclot, in *Fast Ion Transport in Solids*, edited by P. Vashishta (North-Holland, New York, 1979), p. 131.

[6] Aninda Jiban Bhattacharyya, S. Banerjee, T.R. Middya, and S. Tarafdar, Fractals **6**, 285 (1998).

[7] L.O. Griffin, *Physical Constants of Linear Homopolymers* (Springer-Verlag, Berlin, 1986).

[8] S. Chandra, *Superionic Solids, Principle and Application* (North-Holland, Amsterdam, 1981).

[9] R.J. Young and P.A. Powell, *Introduction to Polymers*, 2nd ed. (Chapman and Hall, London, 1991), p. 262.

[10] P.M. Blonsky, D.F. Shriver, P. Austin, and H.R. Allcock, J. Am. Chem. Soc. **106**, 6854 (1984).

[11] Y.L. Lee and B. Crist, J. Appl. Phys. **60**, 2683 (1986).

[12] S.A. Hashmi, A. Kumar, K.K. Maurya, and S. Chandra, J. Phys. D **23**, 1307 (1990).

[13] Aninda Jiban Bhattacharyya, T.R. Middya, and S. Tarafdar, Pramana, J. Phys. **50**, 205 (1998).

[14] Aninda Jiban Bhattacharyya and S. Tarafdar, J. Phys.: Condens. Matter **10**, 10 931 (1998).