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Dense branched growth of $(SCN)_x$ and ion transport in the poly(ethyleneoxide) NH_4SCN polymer electrolyte

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Poly(ethyleneoxide) complexed with NH_4SCN (NH_4SCN wt. % varying from 0 to 20% corresponding to $[NH_4^+]/[\text{ethyleneoxide}]$ 0 to 0.146) have been studied as a possible ion conducting polymer. Good quality films could be obtained only for low salt concentration (NH_4SCN wt. %=0–5 % or $[NH_4^+]/[\text{ethyleneoxide}]$ is 0 to ≤ 0.031), on which detailed ion transport studies have been carried out. These studies showed that H^+ as well as SCN^- ions are mobile. However, films were rubbery (partly liquidus) for higher salt concentration. It is shown that SCN^- aggregation plays a dominant role. Special conditions were created to obtain dense branched structure of the size 5–10 mm of $(SCN)_x$ in the PEO:NH_4SCN film for 20 wt. % NH_4 SCN.

I. INTRODUCTION

Ion conducting polymers (or polymer electrolytes) have recently attracted great attention for their vast applications in the development of solid-state ionics (for reviews see Refs. 1–9). One of the important classes of polymer electrolytes is "polymer-salt complexes" in which some polar polymers [like polyethylene oxide (PEO), polypropylene oxide (PPO), polyvinyl alcohol (PVA), etc.] are doped with alkali-metal salts, ammonium salts, silver salts, acids, etc., to develop alkali, silver, copper, H^+, etc., ion conducting polymers. A systematic effort to develop proton conducting polymer electrolytes has been undertaken in our laboratory, by doping different polymers like PEO,[10] PESc,[11] etc., with different ammonium salts viz., NH_4ClO_4, NH_4HSO_4, $(NH_4)_2SO_4$, NH_4I, etc. In most polymer electrolytes the anions as well as cations are found to be mobile. It is in this context that Chandra and Chandra[12,13] have recently considered polymer electrolytes as natural framework for growth of large size fractals due to random walk of free anions (or cations) and they successfully grew 2–3-cm large iodine fractals in a PEO:NH_4I polymer electrolyte matrix, in which the mobile I^- aggregates. This study led us to take another ion conducting polymer electrolyte PEO:NH_4SCN for growing ramified structures because in this material H^+ as well as SCN^- are the mobile ionic species,[14] out of which SCN^- is known to form multiplets like $(SCN)_2$, $(SCN)_3$, $(SCN)_4, \ldots, (SCN)_x$.[15]

There are some preliminary reports on the ion transport properties of the PEO:NH_4SCN system.[14,16] Doping PEO with a higher concentration of NH_4SCN is problematic since the resulting complexes turned out to be partly liquidus or gluelike and mechanically unstable. This paper reports detailed ion transport studies for a PEO:NH_4SCN complex (with low salt concentration, i.e., $[NH_4^+]/[EO] \leq 0.031$), for which mechanically stable films could be obtained, and growth of $(SCN)_x$ aggregates in the film with higher NH_4SCN content (i.e., $[NH_4^+]/[EO] \geq 0.103$). It appears that $(SCN)_x$ aggregates are possibly responsible for the problems in the solution casting of the PEO:NH_4SCN films for higher salt concentration.

It may be noted that the present study of ramified pattern growth in PEO:NH_4SCN polymer electrolytes under special conditions closely follow our earlier studies[12,13] on iodine fractal growth in PEO:NH_4I polymer electrolytes. The method is primarily electroless aggregation. Many earlier efforts to experimentally study the growth of fractals and dense branched morphology has been by electrodepositions.[17–21] Dense branched morphologies have also been noted during electrochemical polymerization.[22] Further, there are some reports of metallic fractal growth-deposition using an electroless technique. Okubo *et al.*[23] and Mogi *et al.*[24–28] have succeeded in growing DLA-like structures of many metal (M=Ag, Pb, Au) aggregates by taking an aqueous solution of the metal (M) salt and choosing an appropriate metal (M'=Cu, Zn, Pb) strip seed. These types of metallic depositions were the result of simple redox reactions, because of the difference between redox potentials of M/M_{cation} and M'/M'_{cation}. The aggregation behavior (or growth patterns) of the redox reaction products has been found to be effected by external stimuli which was a magnetic field for the studies carried out by Okubo *et al.*[23] and Mogi *et al.*[24–28]

II. EXPERIMENT

Films of PEO:NH_4SCN polymer-salt complexes were prepared by a solution cast technique. Weighed amounts of PEO and NH_4SCN were taken in different stoichiometric ratios and dissolved in distilled methanol. After 5 h of stirring, the solutions were poured in Petri dishes and left for slow drying. After nearly 10 days of drying, good quality films up to $[NH_4^+]/[EO] \leq 0.031$ have been found on which electrical conductivity measurements were possible; for $[NH_4^+]/[EO] = 0.031 - 0.103$, the gluelike films could be obtained but handling for conductivity studies was difficult; for $[NH_4^+]/[EO] > 0.103$ the complex did not dry even in a month and remained liquidus. To force the drying of the complexes with $[NH_4^+]/[EO] > 0.103$, these films were kept for ~12 h in a vacuum system which could pump up to $\simeq 10^{-6}$ Torr in normal conditions. The complexes did not dry enough even then. Some interesting aggregation phenomenon were seen during pumping and also afterwards when the Petri dishes containing the complexes were stored in a desiccator. Optical micrographs of the aggregating structure have been taken using a LEITZ (CITOVAL 2) optical microscope.

The infrared spectral studies of pure PEO, pure NH_4SCN, and complexes of different compositions have been carried out using a Perkin Elmer IR spectrophotometer (model 883). Aggregate forming species has also been identified using IR spectral data. The total ionic transference number has been studied by the polarization method. For this, a constant dc voltage was applied across the Pt/PEO+NH_4SCN/Pt cell and current flowing through the cell was monitored as a function of time. The initial and final values of current, i.e., i_i and i_f, respectively, were used to calculate the ionic transference number (t_{ion}) as[29]

$$t_{\text{ion}} = \frac{i_i - i_f}{i_i} \ . \tag{1}$$

To get detailed and separate information about cationic and anionic transference numbers and the respective charge-carrying species, Coulometric investigation has been carried out. The details of the experiment are given elsewhere.[30] In brief, a constant current ($\simeq 25$ μA) was passed through the Hg/PEO+NH_4SCN/Hg cell and the volumes of the gases evolved on each side (i.e., on the cathode and anode sides) are monitored as function of total charge passing through the cell. Respective transference numbers have been calculated using the relation

$$t_{\text{ion}} = \frac{2 \times 6.023 \times 10^{23} \times 1.6 \times 10^{-19}}{22\,400 \times Q} V \ , \tag{2}$$

where V is the volume of the gas (at NTP) evolved on respective electrode and Q is the total charge passed through the cell.

The electrical conductivity of the complexes of different compositions at room temperature and in the temperature range 25–120 °C have been studied using complex admittance-impedance plots taken with the help of a computer- (HP 9122) controlled Schlumberger Solartron frequency response analyzer (1250) coupled with a Solartron electrochemical interface (1286).

III. PEO:NH_4SCN SYSTEM WITH LOW SALT CONCENTRATION
($[NH_4^+]/[EO] \leq 0.031$)

Figure 1 shows the IR spectra of pure PEO, pure NH_4SCN, and complexed PEO of different compositions. It is known that in PEO salt complexes, it is the cation which gets attached to the ether oxygen of the polymer chain.[31] In the present case, it is NH_4^+ which would loosely bound with the ether oxygen in case of complexation. The significant changes seen in N-H related peaks in the complexed materials are (i) N-H stretching of NH_4^+ (at 3149 cm^{-1}) is shifted to 3200 cm^{-1}, and (ii) ν_4 bending mode of NH_3 (at 1627.5 cm^{-1}) is shifted to 1640 cm^{-1}. These shifts in the position of N-H related peaks shows that NH_4SCN is getting complexed with PEO.

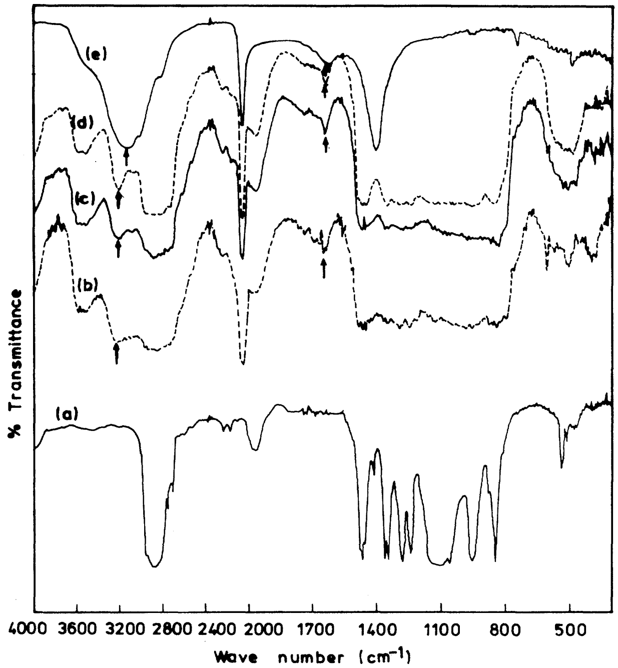

FIG. 1. Infrared spectra of pure PEO, NH_4SCN, and complexed materials of different $[NH_4^+]/[EO]$ ratios: (*a*) pure PEO, (*b*) 0.0059, (*c*) 0.0119, (*d*) 0.0307, (*e*) pure NH_4SCN.

Bulk electrical conductivity of pure PEO and complexed materials have been evaluated using complex impedance plots. Figure 2 shows the bulk conductivity as a function of $[NH_4^+]/[EO]$ ratio. Conductivity is found to increase with increasing salt concentration. This may be attributed to the increased number of charge carriers and also to the increased amorphicity of the system with increasing salt concentration. The percentage of crytallinity as determined by the DTA/DSC measurement[11] is given in Table I which clearly shows that crystallinity decreases (and hence amorphicity increases) with increase in salt concentration.

Figure 3 shows the temperature dependence of conductivity in the temperature range 25°–120 °C. The sudden change in conductivity at ~70 °C may be attributed to the crystalline to amorphous phase transition as indicated by DTA.[11] The $\ln\sigma$ vs $1/T$ plots are Arrhenius both before and after the phase transition:

$$\sigma = \sigma_0 \exp(-E_a/kT) \ , \tag{3}$$

where E_a is activation energy and σ_0 is a preexponential factor. Values of E_a and σ_0 calculated, using data from Fig. 3, are shown in Table I. It may be noted that activation energies are lower for the amorphous region (i.e., above T_m) as compared to that of the semicrystalline region (i.e., below T_m) because of the possible ease with which the ions can move in the amorphous phase.

TABLE I. The values of % crystallinity and Arrhenius conductivity parameters for different PEO:NH_4 SCN films.

$[NH_4^+]/[EO]$ ratio	% crystallinity	Before Tm Ea (eV)	Before Tm σ_0 (S cm^{-1})	After Tm Ea (eV)	After Tm σ_0 (S cm^{-1})
0.0059	83	0.85	2.9×10^7	0.30	31
0.0119	80	0.83	3.7×10^7	0.37	49
0.018	69				
0.0243	69				
0.0307	52	0.59	4.2×10^3	0.36	2.7×10^2

The above bulk conductivities are principally ionic can be shown by Wagner's polarization experiment which essentially determines the total t_{ion}. The cell geometry used was Pt/PEO:NH_4SCN/Pt. Figure 4 shows the current vs time plot under dc polarization. The t_{ion} calculated using Eq. (1) is found to be $\simeq 0.99$. This result shows that the PEO:NH_4SCN complexes are ionic conductors. For determining the cationic and anionic transference numbers separately, coulometric investigation has been carried out. Figure 5 shows the volume of gas evolved at the cathode (due to cation mobility) as a function of total charge flowing through the cell. The value of t_{ion} calculated from the plot, using Eq. (2), is found to be $\simeq 0.81$. The gas is tested by gas chromatography and is found to be H_2 showing that H^+ is the cation taking part in the electrical transport. The anion contribution (due to possible motion of SCN^-) to the total ionic transference number can be had from the knowledge of total t_{ion} and t_{cation}:

$$t_{\text{anion}} = t_{\text{ion}} - t_{\text{cation}} \ . \tag{4}$$

t_{anion} thus evaluated comes out to be $\simeq 0.18$. This is a substantial anionic transference number.

IV. PEO:NH_4SCN SYSTEM WITH HIGHER SALT CONCENTRATION ($[NH_4^+]/[EO] > 0.103$)

As pointed out earlier, the complexes of $[NH_4^+]/[EO] \geq 0.031$ did not dry even in high vacuum. The films always remained gluelike. But the vacuum drying has initiated the aggregation phenomenon and circular aggregates have been found grown in these complexes. A photograph of a full Petridish with so-grown aggregates is shown in Fig. 6(a). A simple hypothesis can be proposed at this stage that some tiny droplets of "nonvolatile liquid" are trapped in the polymer matrix. The force applied by the sucking action during vacuum drying tries to pull "the droplets" upwards which were embedded within the polymer matrix. This process results in a circular nucleation with a little bit thicker center tip, as shown in Fig. 6(b). The growth of these circular nu-

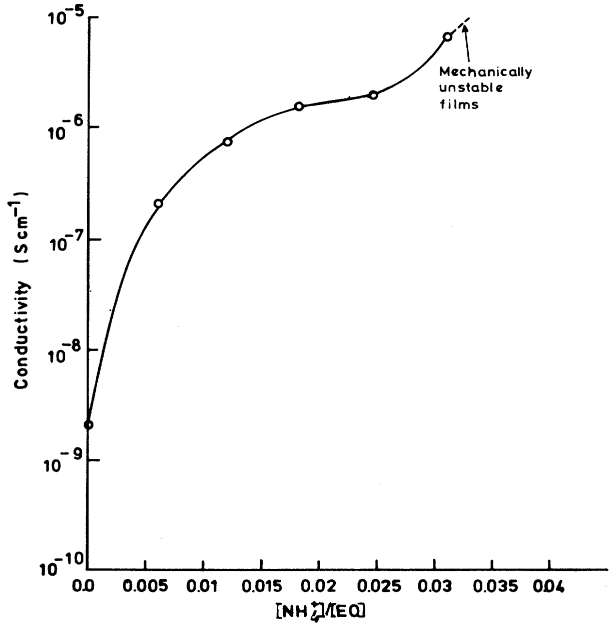

FIG. 2. Composition ($[NH_4^+]/[EO]$) dependence of conductivity of PEO:NH_4SCN complexes.

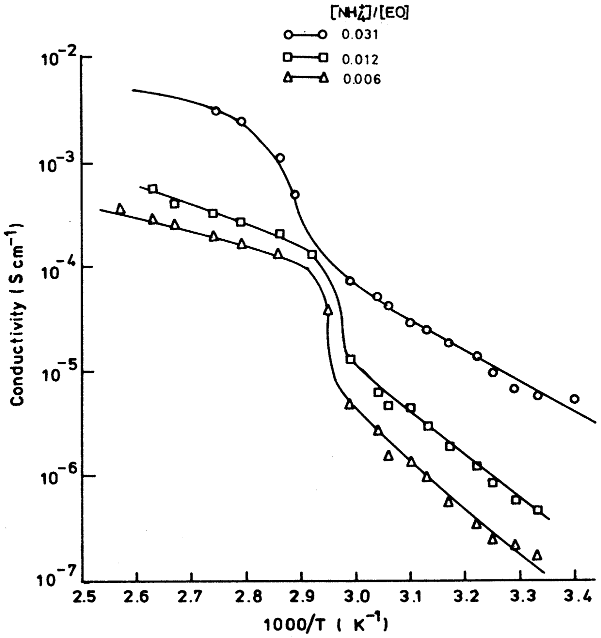

FIG. 3. Conductivity vs $1/T$ plots for PEO:NH_4SCN films of different compositions.

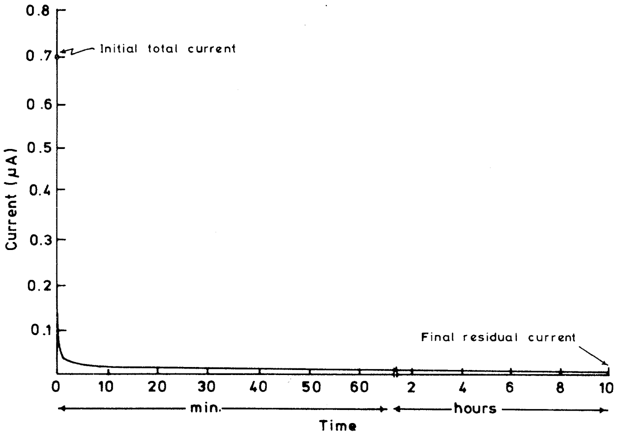

FIG. 4. Wagner's polarization (current vs time) plot at $V = 0.5$ V for a complex having $[NH_4^+]/[EO] \simeq 0.031$.

cleates was monitored with time under a polarizing microscope. After a few days, these aggregates showed ramified growth resulting in dense branched morphology. These ramified structures are embedded in the polymer film with its center tips thicker (but less than the film thickness) in comparison to other parts of the aggregates.

We noted that the growing dense branched patterns are packed too closely when too many aggregates were initially present [as shown in Fig. 6(a)]. Therefore, for obtaining a well-separated dense branched morphology, pumping was stopped just when one or two aggregating centers visually "appear" to have grown. Afterwards, these complexes were left in a desiccator and the growth was monitored. The pattern seen after 2 weeks of storage in the desiccator is shown in Fig. 7. Figure 8 shows the magnified views of the aggregates. Simple logic and IR spectral studies helped us to identify the aggregate-forming species. In the polymer electrolyte PEO:NH_4SCN both the cation (H^+) and anion (SCN^-) are mobile. The aggregating H^+ (if any) would result in H_2 gas and hence the visible aggregates due to H^+ can be ruled out. However, SCN^- is able to make multiplets as $(SCN)_2, (SCN)_3, \ldots, (SCN)_x$ (Ref. 15) and may be the probable species forming the aggregates. To confirm this we carried out IR measurements of materials taken from two portions of the films where (a) no aggregation had taken place and (b) aggregation had taken place. Figure 9 shows the IR spectra of pure PEO, pure NH_4SCN, and the two different portions of the complex. A new peak at 620 cm^{-1} is present in the spectra of the (b) portion of

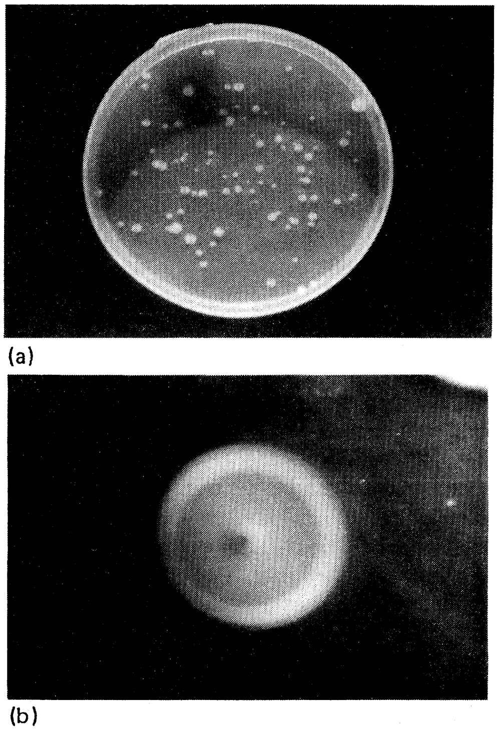

FIG. 6. (a) A typical photograph of a Petridish (diameter $= 7.5$ cm) containing a complex with $[NH_4^+]/[EO] \simeq 0.146$ after vacuum drying. (b) Micrograph of a circular nucleation center obtained in the complex with $[NH_4^+]/[EO] \simeq 0.146$ (mag. = 1.25) after vacuum drying.

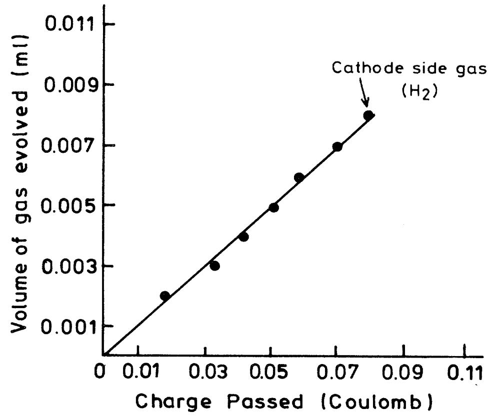

FIG. 5. Volume of the gas evolved on the cathode side as a function of total charge passing through the Hg/PEO:NH_4SCN/Hg cell.

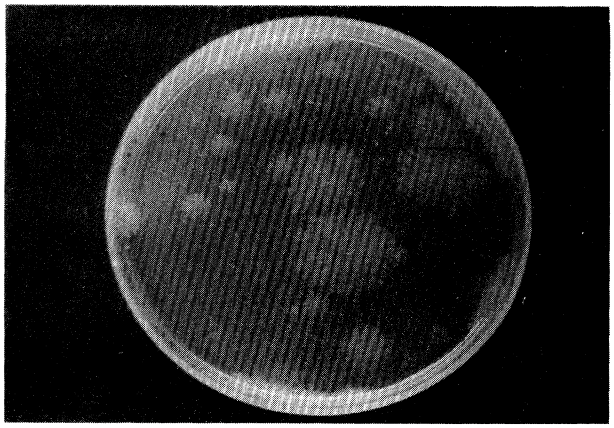

FIG. 7. Aggregate grown in a Petridish (diameter of Petri dish $= 7.5$ cm) in a complex having $[NH_4^+]/[EO] \simeq 0.146$.

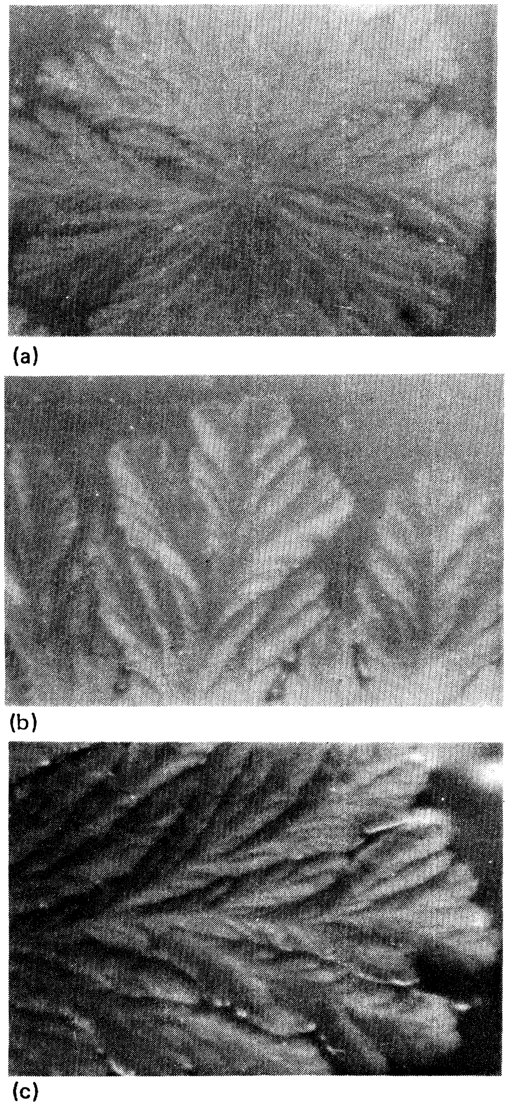

FIG. 8. Magnified optical micrograph of one of the aggregates shown in Fig. 7, (a) full aggregate (mag. = 3.2), (b) and (c) branches (mag. = 6.2).

the complex. This new peak may be attributed to C-S stretching of the thiocyanogen.[32] Hence, we can say that the aggregates are formed by the multiplets of SCN^-. The determination of exact multiplet of SCN^-, which is forming the aggregate, is not possible.

Transport studies in these complexes were not possible because of the mechanical problem (initially complex remains liquidus and films are not formed and after aggregation the films crumble). However, it is expected that grain boundary conduction will be introduced after aggregation, as it was confirmed by Chandra and Chandra[12] in the case of fractal growth in a $PEO:NH_4I$ (with dispersed Al_2O_3) system. We expect the introduction of electronic conduction, also, after the aggregation because of the presence of $(SCN)_x$.[33]

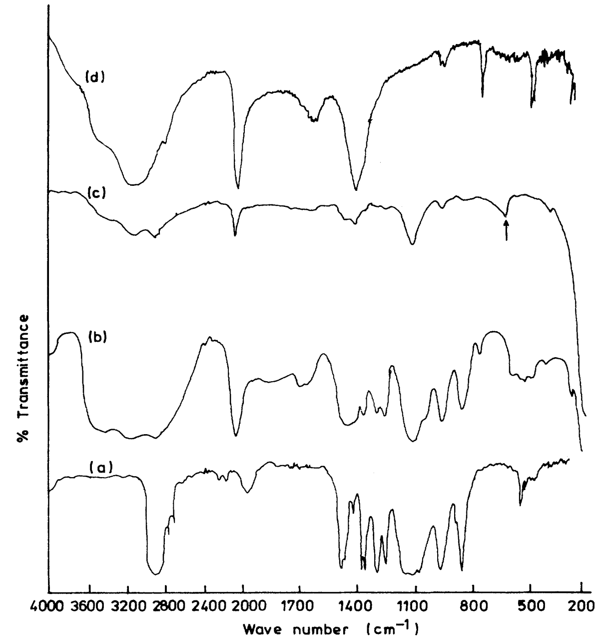

FIG. 9. Infrared spectra of (*a*) pure PEO, (*b*) the portion of complex where no aggregation has taken place, (*c*) the portion of the same complex where aggregation has taken place, and (*d*) pure NH_4SCN.

V. CONCLUSION

$PEO:NH_4SCN$ complexes are basically proton conductors ($t_{H^+} \simeq 0.81$) with a small anion conduction ($t_{SCN^-} = 0.18$). Mechanically stable films could be obtained only up to $[NH_4^+]/[EO] \simeq 0.031$. Above this concentration the films could be prepared but were not mechanically strong enough for use. The complexes having $[NH_4^+]/[EO] > 0.103$ remain liquidus and on pumping and subsequent storage in the desiccator, we have observed the interesting phenomenon of dense branching aggregation. The results indicate that the formation of initial aggregating multiplet of $(SCN)_2$, which is a liquid at room temperature, may be responsible for the problem related with the nondrying of the complexes of $PEO:NH_4SCN$ with high $[NH_4^+]/[EO]$ ratios.

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[1] *Polymer Electrolyte Reviews 1,* edited by J. R. MacCallum and C. A. Vincent (Elsevier Applied Science, London, 1987).

[2] *Polymer Electrolyte Reviews 2,* edited by J. R. MacCallum and C. A. Vincent (Elsevier Applied Science, London, 1989).

[3] *Second International Symposium on Polymer Electrolytes,* edited by B. Scrosati (Elsevier Applied Science, London, 1990).

[4] J. Przyluski, *Conducting Polymers—Electrochemistry* (Sci-Tech, Vadus, Liechtenstein, 1991).

[5] M. B. Armand, Annu. Rev. Mater. Sci. **16**, 245 (1986).

[6] M. Gautheir, M. Armand, and D. Muller, in *Electroresponsive Molecular and Polymeric Systems,* edited by T. A. Skotheim (Marcel Dekker, New York, 1988), Vol. 1, p. 42.

[7] M. Watanabe, in *Solid State Ionics—Materials and Applications,* edited by B. V. R. Chowdari, S. Chandra, Shri Singh, and P. C. Srivastava (World Scientific, Singapore, 1992), p. 149.

[8] J. R. Owens, in *Superionic Solid and Solid Electrolytes—Recent Trends,* edited by A. L. Laskar and S. Chandra (Academic, New York, 1989), p. 131.

[9] S. Chandra, K. K. Maurya, and S. A. Hashmi, in *Recent Advances in Fast Ion Conducting Materials and Devices,* edited by B. V. R. Chowdari, Q. Liu, and L. Chen (World Scientific, Singapore, 1990), p. 549.

[10] S. Chandra, in *Proceedings of the Fifth Asia-Pacific Physics Conference,* edited by S. P. Chia, K. S. Low, M. Othman, C. S. Wang, A. C. Chew, and S. P. Moo (World Scientific, Singapore, 1992), p. 704.

[11] Neelam Srivastava, Ph.D. thesis, Banaras Hindu University, Varanasi, India, 1993.

[12] A. Chandra and S. Chandra, Phys. Rev. B **49**, 633 (1994).

[13] A. Chandra and S. Chandra, Current Sci. **64**, 755 (1993).

[14] D. Prusinowska, W. Weiczorek, H. Wycislik, and J. Przyluski, Solid State Ion. **72**, 152 (1994).

[15] S. S. Bhatnagar, P. L. Kapur, and B. D. Khosla, J. Indian Chem. Soc. **17**, 529 (1942).

[16] M. Stainer, L. C. Hardy, D. H. Whitmore, and D. F. Shriver, J. Electrochem. Soc. **131**, 784 (1984).

[17] M. Mukherjee, S. K. Saha, and D. Chakravorty, Appl. Phys. Lett. **63**, 42 (1993).

[18] E. Ben-Jacob and P. Garik, Physica D **38**, 16 (1989).

[19] D. Barkey, J. Electrochem. Soc. **138**, 2912 (1991).

[20] R. M. Brady and R. C. Ball, Nature **309**, 225 (1984).

[21] I. Mogi, M. Kamito, S. Okubo, and G. Kido, Physica B **201**, 606 (1994).

[22] J. H. Kaufmann, A. I. Nazzal, and O. R. Melroy, Phys. Rev. B **35**, 1881 (1987).

[23] S. Okubo, I. Mogi, and Y. Nakagawa, Sci. Rep. Ritu A, **38**, 383 (1993).

[24] I. Mogi, S. Okubo, and Y. Nakagawa, J. Phys. Soc. Jpn. **60**, 3200 (1991).

[25] I. Mogi, S. Okubo, and Y. Nakagawa, J. Cryst. Growth **128**, 258 (1993).

[26] I. Mogi, S. Okubo, and Y. Nakagawa, in *Proceedings of the Second International Symposium on Electrochemical Processing of Tailored Materials,* edited by R. C. Alkire, N. Masuko, Y. Ito, D. R. Sadoway, and D. J. Economou (Electrochemical Society, New York, 1993), Vol. 93-12, p. 136.

[27] S. Okubo, I. Mogi, G. Kido, and Y. Nakagawa, Fractals **1**, 425 (1993).

[28] I. Mogi, S. Okubo, G. Kido, and Y. Nakagawa, Fractals **1**, 475 (1993).

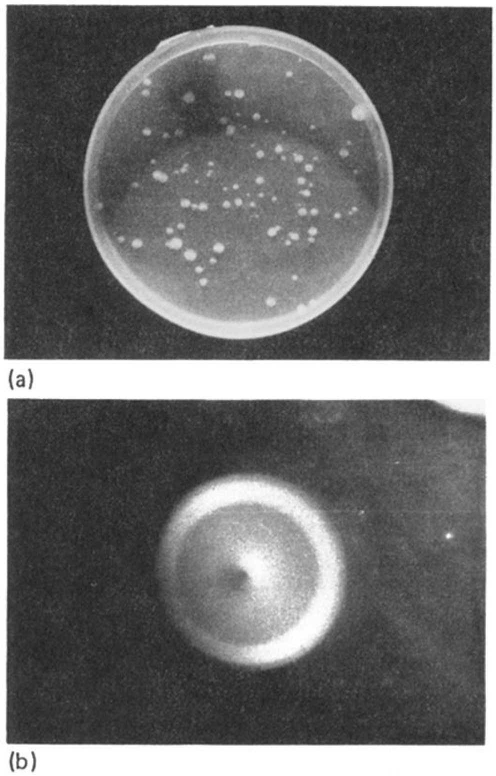
[29] S. Chandra, *Superionic Solids—Principles and Applications* (North-Holland, Amsterdam, 1981).

[30] S. Chandra, S. K. Tolpadi, and S. A. Hashmi, J. Phys. Condens. Matter **1**, 9101 (1989).

[31] Y. Chatani and S. Okamura, Polymer **28**, 1815 (1987).

[32] M. J. Nelson and A. D. Pullin, J. Chem. Soc. Pt. I, 604 (1960).

[33] K. Conheeney and P. V. Wright, Poly. Comm. **27**, 364 (1986).



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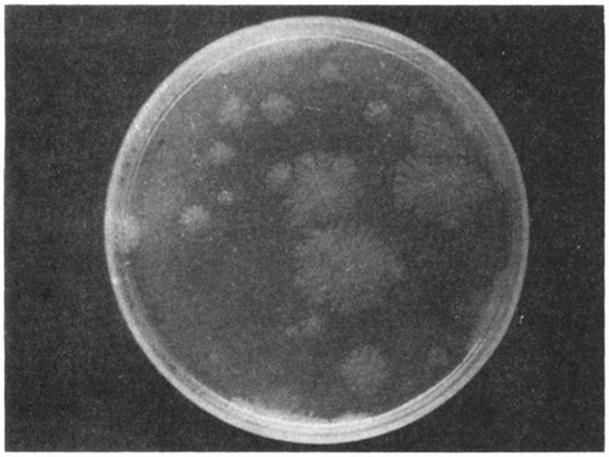

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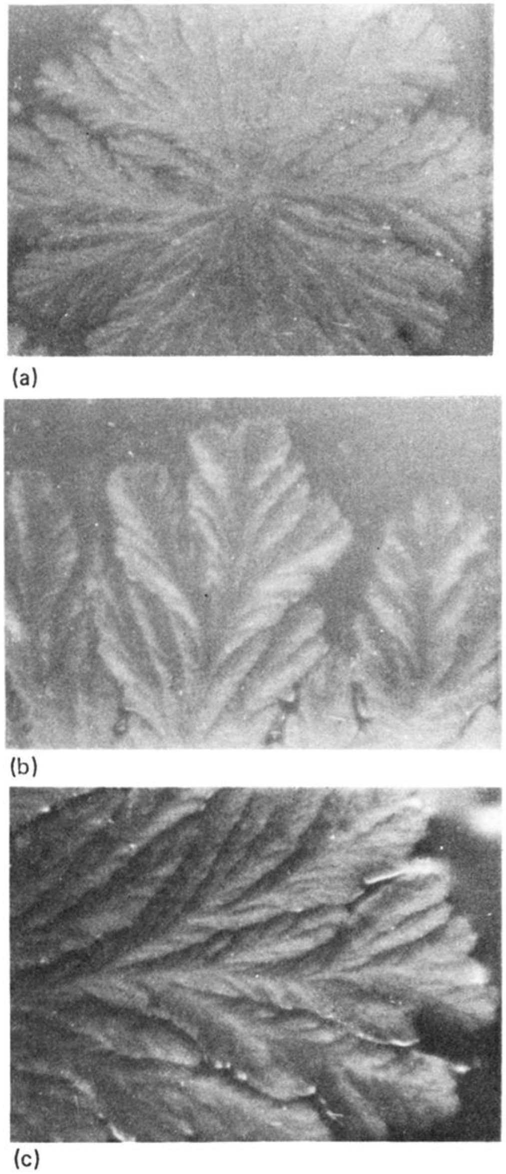

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