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PREPARATION AND ELECTRICAL CONDUCTIVITY OF IODINE DOPED POLYACRYLAMIDE - CUPRIC CHLORIDE COMPLEX

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The preparation, DC volume conductivity and thermal analyses of crystalline complex of iodine doped polyacrylamide with cupric chloride are described. The highest electrical conductivity (1-10 S/cm), using a four point probe measurement is observed in the plane of polyacrylamide - $CuCl_2$ / I_2 film.

Key words: Polyacrylamide; Cupric chloride; Crystalline complex; Electrical conductivity.

Introduction

Investigation of electronic transport in polymers such as electron [1], charge transfer complex system [2,3], metal chelate [4] and conducting composite [5] has increased significantly over the last three decades.

Higashi *et al.* [6] has earlier reported the preparation of polyacrylamide (PAAm) - Cu^{++} chelate and measured the conductivity before and after modifying the chelate with iodine.

In the present paper we report the reinvestigatin of the above mentioned semiconducting polymer using DTA, optical microscopy and X-ray measurements to show the formation of a complex. However, systematic study has been undertaken to elucidate the structure of the complex by X-ray measurements and NMR.

Experimental

Preparation of polyacrylamide (PAAm). Acrylamide from Merck was used as supplied. Potassium per sulphate from Merck was used as initiator to polymerise acrylamide in water at 45° under nitrogen atmosphere. Molecular weight of the polyacrylamide was determined by viscosity measurements in water using Ostwald Viscometer.

Preparation of PAAm-copper complex. 5 wt % aqueous solution of polyacrylamide (M_w 5 x 10^4) was prepared. Cupric chloride salt obtained from British Drug House (0.1 - 2.0g) was added to 20g of the above polyacrylamide solution and stirred for 8-12 hrs.

Preparation of complexed film. The resulting viscous solution obtained by the above procedure was cast onto a polymethyl methacrylate (PMMA) sheet and air dried overnight. The film (0.2- 0.5 mm thick) was peeled from the PMMA sheet and further dried at 100° for 30-60 mins.

A highly lustrous green film thus obtained was doped with iodine by impregnating the complexed film into a solution of iodine (2g) in acetone (100 ml) for a period of 24-72 hrs. The residual solvent and excess iodine from the doped film was removed under vaccum. It became stiffer and brittle and the lustrous green surface became dull greenish black.

Electrical conductivity measurement. DC electrical conductivity measurements were made by using four-point probe method for surface conductivity. A Signaton model S-301 four-point probe system connected with Hewlett Packard digital multimeter model 3468 A was employed in DC sweeps measurements. The distance between each probe was 1.587 mm and the tip radius of each probe was 1.6 mil. All the electrical conductivity measurements were made on open bench.

Differential thermal analysis (DTA). A Perkin - Elmer 170 differential thermal analyser was used for studying the thermal behaviour of the complexed film. Samples were run from room temperature to 250° at a heating rate of 5°/min. in an inert atmosphere.

Results and Discussion

The polyacrylamide (M_w 5 x 10^4) - cupric chloride complexes with different weight ratios give DTA traces as shown in Fig. 1. The bottom curve (A) is that for pure polyacrylamide. Curve B (polymer-salt ratio 20:1) shows a small endothermic band at 473 k which is not observed in curve A (pure polyacrylamide). As salt content increases, the size of endotherm increases proportionately until a very pronounced peak at 472.7 k is observed in curve E (polymer:salt::1:1) and in curve F (polymer salt ::1:1.5). Appearance of this endothermic peak may be related to the formation of a new crystalline polymeric complex. Melting point of pure cupric chloride salt is 893 k [7].

Curve E (polymer:salt :: 1:1.5) shows an exothermic peak just before the melting point of the complex which may be attributed to some reorganization in the system of polymeric complex or to seperation of salt from the polymeric matrix. This behaviour was also observed in the complex of poly (ethylene oxide) - sodium phenolate and poly (ethylene oxide) - sodium acrylate when excess of salts were used [8,9].

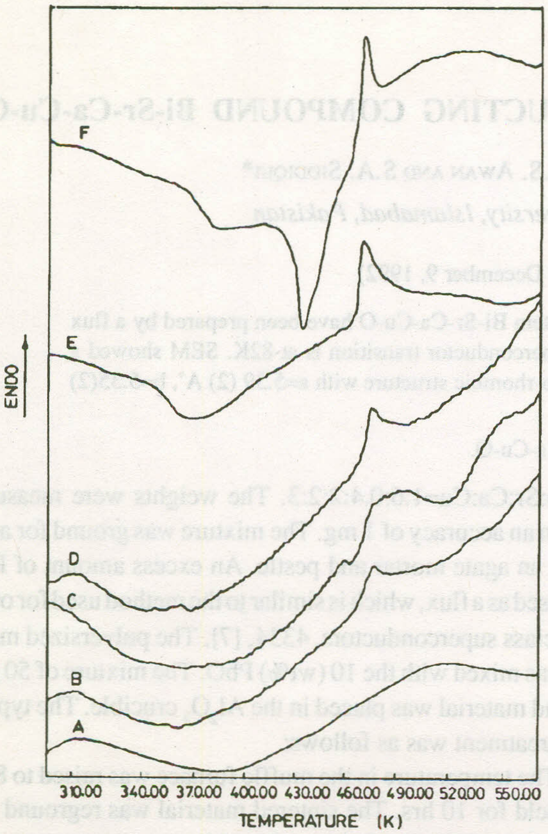

Fig. 1. D.T.A. tracings of PAAm-$CuCl_2$ complexes. (A) Pure polyacrylamide; (B). PAAm: $CuCl_2$ (20:1); (C). PAAm: $CuCl_2$ (10:1); (D). PAAm $CuCl_2$ (2:1); (E). PAAm: $CuCl_2$ (1:1); (F). PAAm $CuCl_2$ (1:1.5).

Inspection of the undoped polyacrylamide-cupric chloride complexed film with polymer-salt ratio ≥1:1.5 using transmitted light optical microscope shows bright crystals on the surface of films which may also be an indication of the seperation of free/excess salt from the polymeric matrix. However, no free crystals were observed onto the surface of the complexed film with polymer-salt ratio ≤ 1:1.

When iodine is absorbed into the complexed film of polyacrylamide-cupric chloride, it is clear from microscopic examination using reflected light that some needle - shaped gold microcrystallites seperate out with polymer-salt ratio ≥ 1:1. Comparison of wide angle X-ray scanning (WAXS) diffraction patterns of the iodine - doped complexed film with iodine - doped salt indicates that the gold microcrystallites are complexed salts having the formula $CuCl_2^{2/3}$ $(I^{-3})_{1/3}$ as suggested by Dupuis *et al* . [10].

Thus, these upper layers are apparently at least partially microcomposite materials. In contrast to the undoped polyacrylamide - cupric chloride complex discussed above, any evidence for complex formation in the doped material is obscured by their optical density and predominance of the phase - seperated salt in WAXS patterns [11].

DC bulk conductivities of iodine - doped films were obtained from I vs V plots using four-point probe surface measurements and two electrodes measurements normal to the film. Carbon/carbon electrodes were used in the latter case over a range of temperature from 25 to 70°. The iodine - doped crystalline polyacrylamide cupric chloride (1:1) gives an approx. linear plot of logσ vs 1/T from ambient temperature upto ca. 70°. Above this temperature, the fall in conductivity may be attributed to the loss of I_2 [11]. Iodine - doped polyacrylamide - cupric chloride films were found to be stable in an ambient atmosphere. A similar film (polymer - salt ratio 1:1) thus exposed for 4-6 months, still showed a conductivity of 10 S/cm.

References

1. J.H. Edwards and W.J. Feast, Polymer Communication, 21, 595 (1980).
2. B. Mussarat, K. Conheeny, J.A. Siddiqui and P.V. Wright, Br. Polymer J., 20, 293 (1988).
3. A.J. Heeger, Faraday Discuss, Chem. Soc., **88**, 203 (1989).
4. H. Kakinoki, O. Sumita, S.C. Cho and F. Higashi, J. Polym. Sci., Polymer Letters Ed., **14**, 407 (1976).
5. A.R. Blythe, *Electrical Properties of Polymer* (Cambridge University Press, Cambridge, U.K., 1979).
6. F. Higashi, S.C. Cho and H. Kakinoki, J. Polym. Sci., Polymer Chem. Ed., **15**, 2303 (1977).
7. R.C. Weast, *CRC Handbook of Chemistry and Physics* (1986-87), 67th ed.
8. J.A. Siddiqui and P.V. Wright, Polym. Comm., **28**, 7 (1987).
9. J.A. Siddiqui and P.V. Wright, Polym. Comm., **28**, 89 (1987).
10. P. Dupuis, S. Flandrois, P. Delhaes and C.P. Coulon, Chemical Comm., 337 (1978).
11. J.A. Siddiqui and P.V. Wright, Faraday Discuss., Chem. Soc. (1989).