Experimental observation of large-size fractals in ion-conducting polymer electrolyte films

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We have succeeded in growing large-size fractals ($\sim 2-3$ cm) in solution-casted ion-conducting polymer films of polyethylene oxide doped with ammonium iodide. These are shown to be "diffusion-limited aggregates" due to iodine ions in random walk. This mechanism is supported by energy dispersive x-ray analysis, x-ray diffraction, optical absorption, polarization, and complex impedance studies.

Many physical, technological, and biological processes exhibit noninteger (or fractal) dimensionality as was recognized by Mandelbrot[1] in his studies on complex geometrical shapes. Fractals are generally observed in far-from-equilibrium growth phenomena, and hence they provide a natural framework for the study of disordered systems. Fractal growth patterns can be seen in nature for example, as mountains, snow flakes, continent shores, branches of trees, etc., in the laboratory (for example in dendrites, electrodeposition of ions, etc., and in mathematical abstractions such as time correlation, density fluctuation, etc. Examples of computer simulation are plentiful, but experimental fractals (particularly large-size fractals) under laboratory controllable conditions are limited in number. There are no experiments where large-size fractals have been due to particles in a random walk without any external stimuli. Fractal experiments on electrodeposition, pattern generation due to chemical reaction, viscous fingering, etc., have shown that apparently large size fractal patterns may be seen. In the electrodeposition experiment, a radial electrical-field geometry was used[2,3] and the ions moving under this stimuli formed, diffusion-limited-aggregate (DLA) patterns at the interface. In the pattern generation on plaster,[4] a part of the interface gets removed due to the dissolution/chemical reaction, and as such this does not conform to the geometry of DLA computer simulation experiments, which generally forms the basis of fractal pattern identification. Here we describe an experiment where large-size fractals ($\sim 2-3$ cm) have been successfully grown and studied without any external stimuli.

The intuitive philosophy of the present experiment is

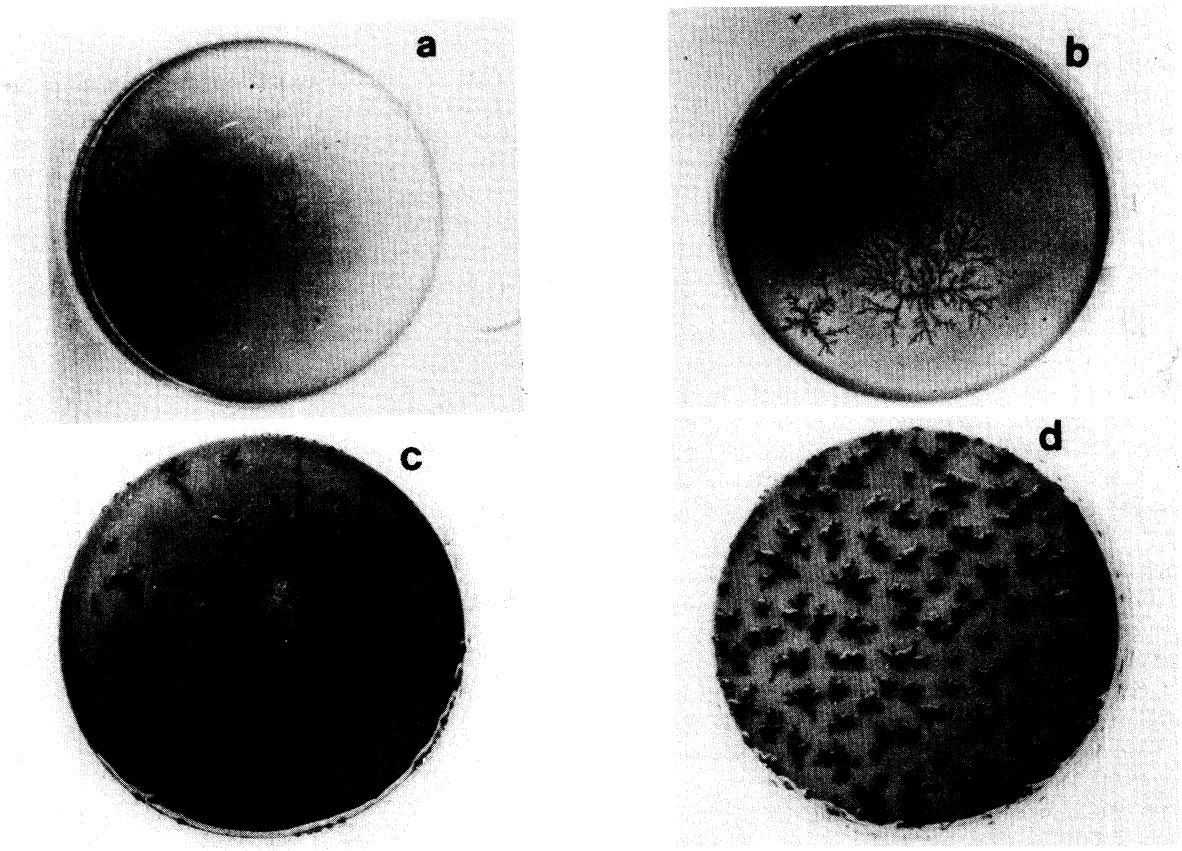

FIG. 1. Optical micrographs of fractals obtained in PEO:NH_4I films of different compositions in 7.5-cm Petri dishes with (a) $NH_4^+/EO=0.20$, 10% of Al_2O_3; (b) $NH_4^+/EO=0.20$, 30% of Al_2O_3; (c) $NH_4^+/EO=0.30$, 20% of Al_2O_3; (d) $NH_4^+/EO=0.30$, 30% of Al_2O_3.

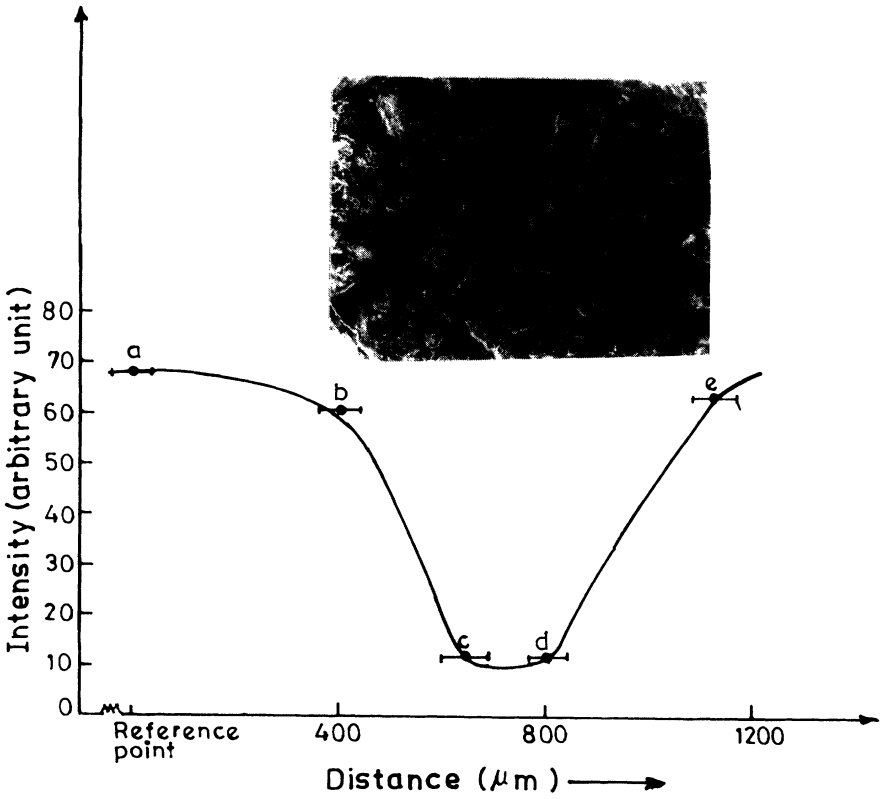

FIG. 2. Intensity of EDAX peak corresponding to iodine at different places in the film with fractals. Inset: scanning electron micrograph of film with fractals for whose regions *a*, *b*, *c*, *d*, and *e* the relative iodine EDAX peak is given in the graph.

as follows: Fractal aggregates (specially diffusion-limited aggregates) involve the random walk of particles and their subsequent sticking. For example, Witten and Sander[5] simulated DLA by computer by taking a seed particle and by launching another particle far from it, carrying out random walks (or diffusing) until it got stuck adjacent to the seed particle. Subsequent particles in similar random walks also coalesce until a large aggregate appears. Experimentally, highly viscous polymer solutions (or even the amorphous regions of polymeric films developing as the solution dries) are good media for random walks provided particles are available to undertake the random walk. Recently, we have been studying polyethylene oxide (PEO) complexed with NH_4X ($X^-=I^-$, ClO_4^-, HSO_4^-, etc.) (Refs. 6–8) in which NH_4^+ loosely bonds with the polymer chain while the anion (X^-) remains outside. These films are ion-conducting polymers permitting both cations and anions to move. For a visual observation, we thought iodine aggregates to be ideal due to the visibly distinct iodine color and so we chose the PEO:NH_4I complex for the present study. In order to increase the number of particles, we used a higher NH_4I concentration in the films during complex formation (and added Al_2O_3 for hardening, when necessary).[9]

PEO (molecular weight $\sim 6\times 10^5$) and NH_4I weighed in desired weight ratios were dissolved in distilled methanol and stirred thoroughly at 40 °C. After allowing sufficient time for complex formation, Al_2O_3 was added while magnetic stirring was continued until a highly viscous mixture was obtained. This was poured in a polypropylene Petri dish for solution casting of the polymeric film. A slow evaporation rate was maintained by keeping the Petri dish closed. After about 3–4 days, tiny nucleated reddish brown aggregates were observed which grew into large-size fractals within a few weeks time. We repeated this 20–25 times and found qualitatively similar features. Figure 1 shows typical optical micrographs of a 7.5-cm-diam Petri dish containing PEO:NH_4I complex for two weight ratios 60:40 [Figs. 1(a) and 1(b)] 50:50

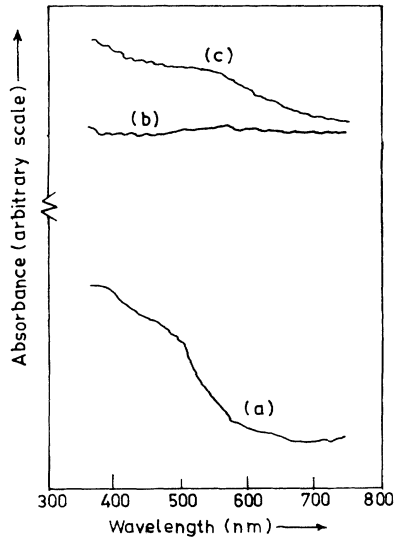

FIG. 3. UV/visible spectra of films obtained by subliming (a) pure iodine, (b) PEO:NH_4I:Al_2O_3 sample with no fractal growth, and (c) PEO:NH_4I:Al_2O_3 sample with extensive fractal growth.

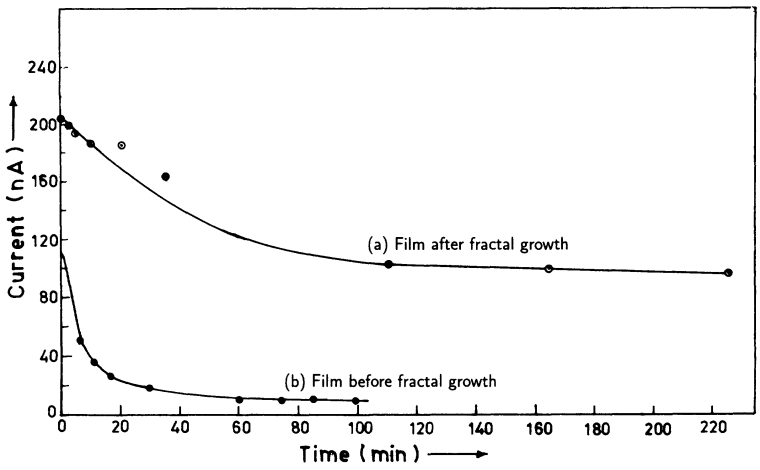

FIG. 4. Polarization curve for film (a) after fractal growth and (b) before fractal growth.

[Figs. 1(c) and 1(d)] corresponding to $NH_4^+/EO=0.20$ and 0.30, respectively, with different amounts of Al_2O_3. The general conclusions are the following.

(i) The number of nucleation centers for fractal growth is higher for higher NH_4^+/EO ratios [see Figs. 1(b) and 1(d)].

(ii) For the same NH_4^+/EO ratio, the number of nucleation centers also depends upon the amount of dispersed Al_2O_3 [compare Figs. 1(a) and 1(b) or 1(c) and 1(d)].

(iii) All the nucleation centers do not grow equally.

(iv) The rate of fractal growth (and ultimate size) is higher if nucleation centers are less [compare Figs. 1(a), 1(c), and 1(d)].

(v) The fractals shown in Figs. 1(a) and 1(c) were used for calculating the dimensionality (D) of the fractal by a well-known procedure.[10] The average value of D was found to be ~ 1.7, which is typical of diffusion-limited aggregates.

One branch of the fractal as seen under a scanning electron microscope is shown as the inset in Fig. 2. Selected-area energy-dispersive x-ray analyses (EDAX) were taken at five places on the fractal arm (a), on the fractal arm (b), not on the fractal area (c), not on the fractal area (d), and on the second fractal arm (e). The intensity of iodine ($L\alpha$) is shown in Fig. 2, which clearly indicates high iodine concentration on the fractal arm.

Some interesting experimental implications of the growth of these iodine fractals have also been studied and are briefly summarized below.

(a) The films (one with extensive fractals and the other with no fractals) were kept in two different Petri dishes covered by a glass cover. The temperature of the Petri dish bottom was raised to 70 °C. If the free form of iodine is present in the film, as conjectered for films with fractals, then it will "sublime" and deposit at the glass

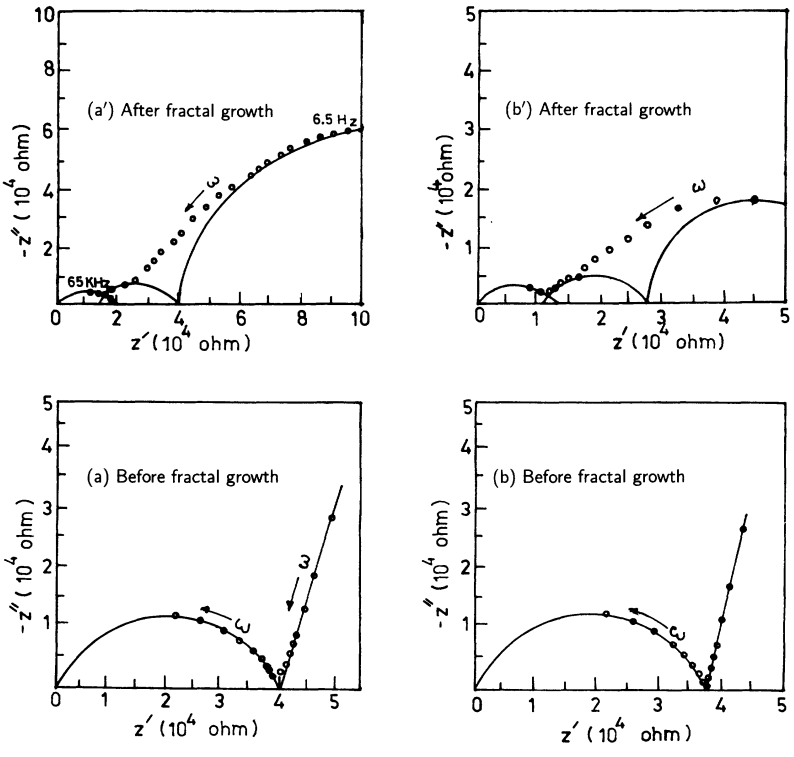

FIG. 5. Complex impedance plots for films before and after fractal growth. (a), (a') are for film with $NH_4^+/EO=0.20$, 10% of Al_2O_3, and (b), (b') are for $NH_4^+/EO=0.20$, 30% of Al_2O_3.

cover which acts as cold finger. No such deposit was found to occur for films with no fractal growth, but we did find a film of violet color forming on the glass cover plate for films with fractals. The optical absorption spectra of this violet film recorded by a Hitachi UV/visible spectrophotometer is given in Fig. 3 and was found to be typical of iodine.

(b) The development of streaks of iodine "fractals" will introduce grain boundaries and regions of electronic conduction. These can be tested by impedance spectroscopy and polarization studies. A typical result of Wagner's polarization experiment (i vs time plot) with blocking electrodes is given in Fig. 4. The ionic transference number (t_{ion}) can be calculated with the help of total current i_T and the final current, which is the electronic current i_e,

$$t_{\text{ion}}=(i_T-i_e)/i_T, \quad t_e=i_e/i_T \ .$$

The ionic and electronic transference number calculated from these curves[11] are $t_{\text{ion}}=0.92$, $t_{\text{elec}}<0.08$ for films with no fractals, but for films with fractals $t_{\text{ion}}=0.54$, $t_{\text{elec}}<0.46$. This shows that electronic conduction has been introduced.

(c) Grain boundary effects in ionic conductors can be separated out by impedance spectroscopy.[11] The real (Z') and imaginary (Z'') parts of the impedance were measured by a Solartron impedance analyzer (1250 FRA and 1286 ECI) in the frequency range 6.5 Hz–65 kHz. Typical plots are shown for two films (before and after fractal growth). The impedance plots [Figs. 5(a) and 5(b)] before fractal growth consist of two semicircles characteristic of electrode-electrolyte and bulk impedances. However, a small third semicircle appears in impedance plots of films after fractal growth, which is due to the grain boundary contribution.

(d) The films were also examined by x-ray diffraction (XRD). In films with no fractals, the (020) reflection of iodine at $2\theta\cong 24°$ was absent as expected, but appeared in films with fractals. Figures 6(a) and 6(b) give the XRD patterns of the films without and with fractal growth, respectively. Films with more copious fractal growth gave higher peak heights for I_2 (020) reflections as shown in Figs. 6(c) and 6(d).

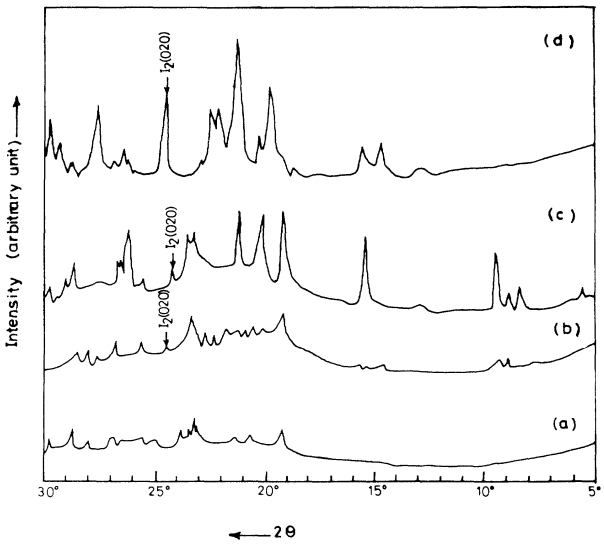

FIG. 6. XRD patterns of films of PEO:NH_4I:Al_2O_3 (a) with no fractal growth, (b) with fractal growth, and (c), (d) with extensive fractal growth.

The important conclusions of this study are the following: Large-size (2–3 cm) DLA-type fractal patterns are observed during solution casting of films of ion-conducting polymers (PEO in the present case complexed with NH_4I). These fractals are principally due to a "random walk and subsequent aggregation" of iodine removed the polymer complex. Addition of Al_2O_3 seems to further help this. This and similar materials can be good systems for different experimental studies on fractal growth.

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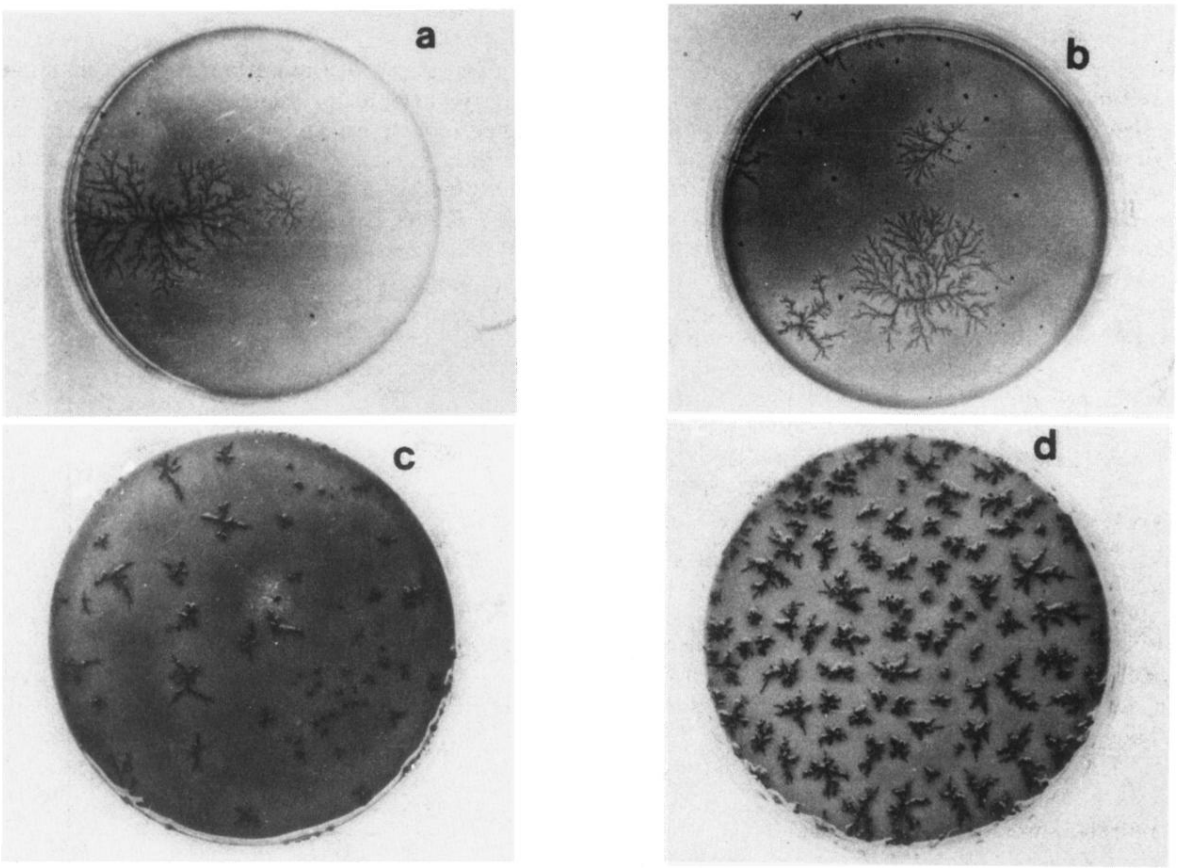

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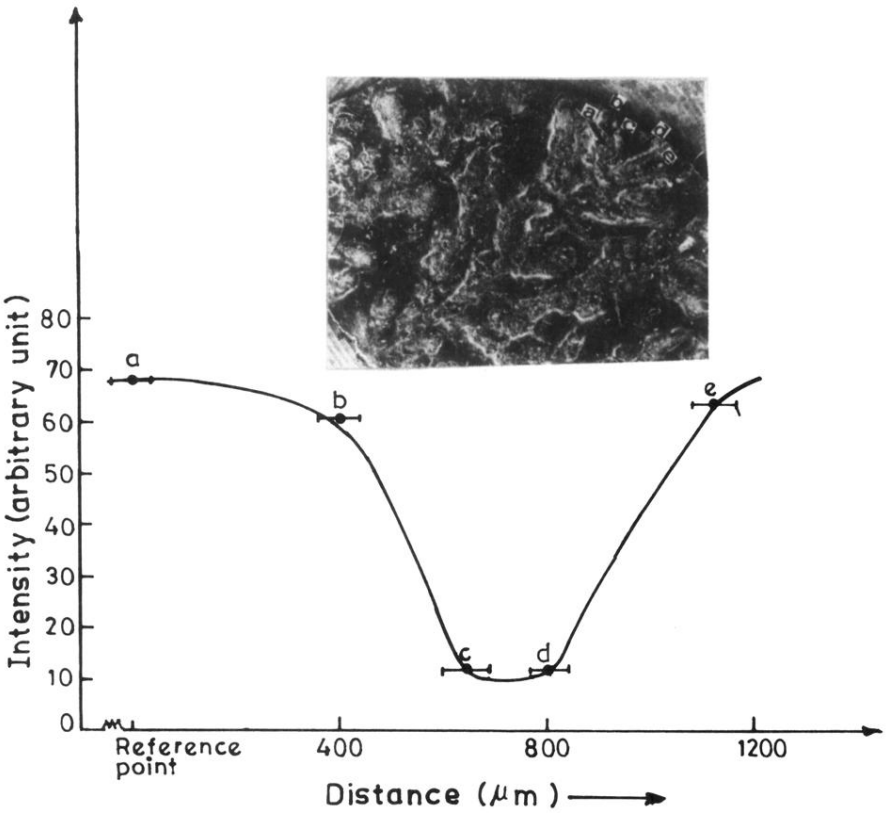

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