Chapter 1
Introduction

1.1 OVERVIEW

Euclidean geometry, the widely known type of geometry, comprises of lines, planes, arcs, cylinders, spheres and others which are smooth and regular ones. However, people have always been fascinated by interesting shapes in nature and common experience (on the length scale of everyday experience at least) suggests that nature favours the formation of rough, irregular shapes rather than smooth regular ones. As Euclidean geometry is based on one, two or three dimensions which are not realistic in nature, therefore, it is impossible to approximate the complex and irregular shape of natural objects with Euclidean geometry. For instance, a general view of a hillock would project a triangular shape in our imagination. But as we take steps closer and closer, we notice the irregularities in that image. We notice that the shape is not wholly triangular but contains irregularities in the form of rocks, bushes, humps, etc. Every step closer brings out more and more details, contradicting the generalization that we had earlier made. It is impossible to describe such objects by traditional Euclidean geometry. Other examples include coastlines [1], dendritic solidification such as alloys and snow crystals [2], distribution of galaxies [3], soot aggregate [4] and lightning patterns [5]. To describe such objects which are too irregular to fit in conventional Euclidean geometry, Mandelbrot in 1975, coined the term “fractal”. Fractal can be thought as a mirror to describe these irregular images. The history of fractals began by the research of Gaston Maurice Julia, who wrote a paper about the iteration of rational function and continued with the findings of Benoit Mandelbrot. Benoit Mandelbrot gave the term “fractal” from “frangere”, a Latin verb, meaning ‘to break’ or ‘fragment’. He was examining the shapes created by Gaston Julia, a mathematician in 1920’s, by iterating a simple equation and mapping these equations in complex plane, where Gaston Julia (who was working without a computer) could not describe these shapes using Euclidean geometry. With the aid of computer graphics, Mandelbrot who worked at IBM’s Thomas J. Watson Research
Center, was able to show how Julia’s work was a source of some of the beautiful fractals known today [6] and were first published in his book *Les objets fractals, forêt, hasard et dimension* (1975) (“The fractal geometry of nature, 1982”) which demonstrates the potential application of fractals in nature and mathematics [7]. Two of the most important properties of fractal are:

- Self similarity
- Non-integer dimension (fractional dimension)

Self similarity means that a component part of the fractal object resembles the whole while non-integer dimension means that the shape is neither 1, 2, or 3-dimensional and it is in fraction greater than the topological dimension of the set, remaining constant whatever the scale. For example, a fern leaf contains patterns that have many irregular shapes and each of these smaller leaves, in turn, is made from smaller leaves and the closer one looks, the more details one can see as shown in figure 1.1.

![Figure 1.1: Fern leaf as an example of nature’s self-similarity](image)

The concept of fractals has attracted interest of scientists in many fields. As cited by Hastings and Sugihara (1993) [8], “the science citation index listed around
400 papers with the word fractal in their title”. They span fields ranging from nature, cosmology and development biology. A lot of research related to the growth and shapes of fractals through theoretical modelling and simulation of pattern formation has been done [9,10,11]. The characteristic feature of many processes in physics, chemistry and engineering is the formation of larger clusters by aggregation [12]. Aggregation occurs when a system of identical particles is joined into clusters according to some rule. Aggregation always leads to ramified structures with fractal geometry [4]. A wide field of study on materials consists of colloids, polymers, aerosols, ceramics, glasses and thin films which are formed by aggregates.

There have also been experimental studies on fractals in polymers which include fractal growth of silver nanocluster within a polymer matrix [13] and crystal pattern formation from dendrites through four fold-symmetric structure to faceted crystals of ultra thin poly(ethylene oxide) films which were carried out by Zhang et al. [14]. Moreover, fractal concept is also encountered in conducting polymers as these polymers grow randomly during polymerization at microscopic level which gives rise to tree like, broad leaf-like structures [15, 16].

Mostly, all these experimental studies have been performed by applying some sort of an external stimuli (like electric field, magnetic field, pressure etc.) which gives rise to very small sized (micron sized) fractal patterns. However, large size fractal patterns (~3-4 cm) under bias free condition (i.e., without external stimuli) was first reported in polymer electrolyte (alkali-metal salt dissolved in polyether based polymer) membranes by Chandra and Chandra [17, 18, 19, 20]. The observation of fractal pattern formation in polymer electrolyte films has new avenues for detailed studies of growth due to the slow growth rate. Chandra and Chandra provided interesting perspective to the study of fractal growth in ion conducting polymer electrolyte membranes. According to them, growth was principally due to random walk of ions and their subsequent aggregation. The polymer acted as a host and the inorganic salts dissociated and provided random walkers for aggregation to take place around nucleation sites. They also did the experimental simulation of many theoretical models using polymer electrolyte as a medium [18, 19]. Experimental simulation of
fractal patterns in which random walkers were of non-uniform size (i.e., there was a particle size distribution) as computer simulated by Ossadnik et al. [21] has also been done by them. They used UV photolysed DNA as a system to give non-uniform particle size distribution [22] and subsequent aggregation.

Recently, another group of researchers also cultured fractals in various ion conducting polymer electrolyte membranes experimentally. They also did theoretical modelling of the experimentally cultured fractals [23, 24, 25, 26].

Thus, the observation of fractal pattern formation in polymer electrolyte films gives a platform for detailed studies of the kinetics of growth due to ion motion in polymer electrolyte that are kept apart by cumblic repulsion and kept afloat by Brownian motion leading to network formation. However, many aspects related to the mechanism of network formation remain puzzling because arguments are at phenomenological stage.

1.2 FRACTALS AND FRACTAL GEOMETRY

Fractals, as these geometric shapes are called, can be split into parts and each part is a smaller replica of the whole. Fractals are not only man made but are also widely seen in nature. Euclidean geometry provides concise accurate description of man-made objects but is inaccurate for natural shapes as they are random. Machine shops give Euclidean geometry objects as these objects are easily built. According to Kaye [27], there are limitations in trying to approximate the shape of natural object with Euclidean geometry. Thus, Euclidean geometry is unable to describe the irregularity in shape shown by natural objects which are complex, irregular at all levels of magnitude and their structure is indefinite. According to Connor [28], fractal geometry is a new language to describe, model and analyze complex forms found in nature. Fractal geometry is the extension of conventional Euclidean geometry and occupies a borderline place between linear geometry and complete randomness. According to Deering and West [29], the shape in fractal geometry is far closer to nature compared to Euclidean geometry.
Therefore, it can be said that there are two types of geometries:

- Euclidean
- Non-Euclidean

Euclidean geometry elements include plane and solid geometry, advanced arithmetic, algebra, trigonometry, descriptive geometry, projective geometry, analytical geometry and differential geometry.

Non-Euclidean geometry includes hyperbolic geometry, elliptic geometry and fractal geometry. Fractal geometry has been created by mathematicians depicting the universe beyond the boundaries of Euclidean geometry. Table 1.1 lists the major differences between Euclidean geometry and fractal geometry.

**Table 1.1: Difference between Euclidean and fractal geometry**

<table>
<thead>
<tr>
<th>Euclidean geometry</th>
<th>Fractal geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional (&gt; 2000 years)</td>
<td>Contemporary (35 years)</td>
</tr>
<tr>
<td>Defined by characteristics size or scale</td>
<td>Scale free (no specific scaling)</td>
</tr>
<tr>
<td>Suits man-made objects</td>
<td>Appropriate for natural shapes (random, statistical or stochastic)</td>
</tr>
<tr>
<td>Described by simpler formula</td>
<td>Recursive algorithm</td>
</tr>
</tbody>
</table>

A unique difference between fractal and Euclidean objects is that for Euclidean objects, their length is constant regardless of the length of the measuring device while the fractal contour increases with increasing length of the measuring device. In other words, a marked difference between Euclidean shapes and fractal shapes is that ‘perfect’ fractals have a structure which is said to be self-similar or independent of length scale whereas, Euclidean shapes have a characteristic scale. The fractal object is characterized by a constant parameter called the fractal dimension (D). Fractal dimension (D), therefore, serves as a quantifier of complexity, an increase in D represents an increase in complexity.
1.2.1 Self-similarity

As previously mentioned, self-similarity, scale independence, irregularities and complexities are the main characteristics of the fractal geometry. Self similarity is a property having which means that, when a small portion of an object is similar to the whole object, reiteration of irregular details or pattern occurs at progressively smaller scale. Self similar features remain invariant under changes of all scales, i.e., scaling symmetry. This means that a self similar structure is infinitely complex because of its similarity at all levels of magnification. For an observable \( A(\chi) \), which is function of variable \( \chi \): \( A = A(\chi) \) obeys the scaling relation

\[
A(\alpha \chi) = \alpha^s A(\chi)
\]  

(1.1)

where, \( \alpha \) is a constant factor and \( s \) is a scaling exponent which is independent of \( \chi \).

Consider an object \( A \) formed by a set of points \( \chi = \chi_1, \chi_2, \ldots, \chi_n \) in \( n \)-dimensional space with a scaling factor \( r \) which changes the coordinates to \( r \chi = r\chi_1, r\chi_2, \ldots, r\chi_n \). The object is self similar with respect to the scaling factor \( r \) if \( A \) is the union of \( N \) non-overlapping subsets \( A_1, A_2, \ldots, A_n \) and each of which is congruent to the set \( r(A) \) obtained from \( A \) by the similarity transform with \( 0 < r < 1 \) [30]. Here, congruent means that \( A_i \) is identical to \( r(A) \) after possible translations. There is also another form of similarity called anisotropic self-similarity or self affinity. Power law description for self similar objects is isotropic (i.e., changing the scale or resolution in one direction changes the system uniformly in every spatial direction) while self affine objects have anisotropic rescaling or direction dependent scaling. Affine transformation is a transformation that sends a point \( \chi = \chi_1, \chi_2, \ldots, \chi_n \) in the new point \( r \chi = r_1 \chi_1, r_2 \chi_2, \ldots, r_n \chi_n \) where the coefficients \( r = r_1, r_2, \ldots, r_n \) are not necessarily all equal, i.e., different scaling factors \( r = r_1, r_2, \ldots, r_n \) for different directions. A set is said to be self affine with respect to a ratio vector \( r \) if it is congruent with its image under the affine transformation \( r \). An example of deterministic self affine curve is shown in figure 1.2. As shown in figure 1.2, an isotropic rescaling of a piece of the shape does not match the previous iteration.
Figure 1.2: Deterministic construction of self-affine curve. In the first iteration, the diagonal in figure (a) is divided in four equal parts and replaced by the structure shown in figure (b). Figure (c) shows the repetition of the same procedure in all four segments. If the section in the dotted box is rescaled isotropically, what is shown in the right, is different from the shape in the previous iteration [30].

Self similarity is the main characteristic in defining fractals and it is one of the crucial properties in differentiating between the ideal and natural fractals [31].

Natural features display statistical self-similarity; their statistical properties remain scale invariant over a specified but limited range of scales. According to Thatcher [32], natural objects are randomly generated rather than exactly or are scale symmetric. This means that a natural rough shape revealed at one particular magnification only bears an approximate similarity to the shape at another level of magnification, that is, natural object’s fractal properties are within an upper and lower bound. For example, a coastline is also a self similar natural fractal but it does not have perfect self similarity. As an illustrative example in figure 1.3, the fractal coast is given which is a self similar structure. Starting from the upper left image, by magnifying its central part (with in white box), after six iterations exactly the same initial structure is obtained. That means, this structure is self similar having infinite
complexity [33]. According to McNamee [34], the distribution shapes at different levels of magnification is known as self affinity. In conclusion, there are two main contributors to the statistical self-similarity behaviour in natural fractals which have upper and lower limit bounds and also self affinity.

Artificial fractals are geometrically self similar. Geometric similarity is a property of space time metric and has been known from centuries. These are based in equations that undergo iteration, a form of feedback based recursion. Subsets of geometric fractals (i.e., mathematical fractal (artificial fractal)) are infinitesimal subdivisional and each subset (however small) contains no less detail than the complete subset. Examples are von Koch curve, the Sierpinski triangle and the Cantor set, these examples are briefly discussed in section 1.2.4.

![Fractal coast, repeating after 6 magnifications, R. F. Voss [33]](image)

**1.2.2 Fractal dimension**

Fractal dimension is a measure of how “complicated” a self-similar figure is and it is usually in fraction. Fractal dimension implies the scope to which fractal object fills the Euclidean dimension in which it is embedded and it is usually non-integer. For instance, the dimension of coastline appears to be one, it is just a wiggly line. On the
other hand, it is so twisted that it fills more of 2-dimensional rectangle than a straight line. The purpose to measure the dimension is to distinguish different fractals. Although all fractals have their own fractal dimensions, these are not same as the familiar Euclidean dimensions. There are several notions of dimensions which are related to fractal dimension such as topological dimension and Hausdroff dimension. According to Maurice [35], Hausdroff dimension is an extended non-negative real number, that is, a number in the closed infinite interval \([0, \infty]\) associated to any metric space. Topological dimension is a basic concept of dimension, a point has a 0 dimension, line has 1 dimension, plane has 2 dimensions and organisms move in 3-dimensional spaces [36]. Finally, mathematical fractal is defined as any series for which Hausdroff dimension (a continuous function) exceeds the discrete topological dimension.

Fractal dimension can be obtained using a relationship between the number of copies and the scale factor. Scale invariance is a fundamental property behind many power laws with non integer scaling exponents observed in nature. The kind of law which is relevant, as explained previously, is a power law of the form

\[
t = c \cdot h^D
\]

(1.2)

It is called power law because \(t\) changes as if it was a power of \(h\). Taking logarithmic on both sides of the equality sign, we obtain:

\[
\log t = \log c + D \cdot \log h
\]

this implies that

\[
D = \frac{\log \left(\frac{t}{c}\right)}{\log h}
\]

(1.3)

It is a statistical quantity which gives an indication of how completely a fractal appears to fill space as one zooms down to finer and finer scales.

Fractal dimension is not easy to understand. The details are confusing even for a research mathematician [33]. The methods of determining it are discussed below and we restrict ourselves to an elementary discussion of the suitable methods, one of which has been selected to be used in our study [33].
1.2.2.1 Richardson method

In early 1960s, Richardson method devised by Louis Fry Richardson was one of the earliest methods to measure fractal dimension. It started when Richardson asked a question ‘How long is the coast of Great Britain” [27] and thus, invented a method to estimate the coastline of Great Britain. As shown in figure 1.4, a polygon is used to estimate the perimeter of coastline of Great Britain. Using this technique a coast perimeter is measured with side lengths of polygon ($\lambda_1, \lambda_2, \lambda_3$) of different polygons and then, by determining its slope, the corresponding dimension was calculated.

![Figure 1.4: Richardson method used to estimate the coastline of Great Britain [27]](image)

However, the Richardson method slightly underestimates the length as it tends to enclose the outermost points of the structure's boundary [37]. As a result, the underestimate of boundary perimeter severely influences the calculation of the fractal dimension.

1.2.2.2 Mass radius method

The next method is the mass radius method also known as the Scholl method. The fractal dimension is computed by measuring the mass $m$ in a circle of radius $r$ starting from the center of the set. It yields fractal dimension following the proportionality:
where, \( m(r) = \frac{M(r)}{M} \) is the ‘mass’ within a circle of radius \( r \),

\[ M(r) = \text{data set of points contained within a circle} \]

\[ M = \text{total number of points in the set} \]

If the set is fractal, the graph is a straight line with a positive slope equal to \( D_m \) [38]. This method studies structure in radial fashion such as dendritic growth in radial axis.

### 1.2.2.3 Box counting method

The final method is the box-counting method which is one of the best method, easiest to perform and favourite among most researchers for calculating the fractal dimension [33]. This method can be used to analyze irregularities in surface filling space volume and suitable for images, however complex. According to Longley [39], the box counting method can be used to measure the fractal dimension of a curve. Furthermore, according to Peitgen [40], the method can be applied to overlapping curves and structures lacking strict self-similar properties.

The method is obtained by covering a geometric figure by square meshes of side ‘\( r \)’. The magnitude of the square side ‘\( r \)’ is changed at each step. Then, if \( N(r) \) is the total number of such boxes required to cover the whole object, the total length is given by:

in 1-D:

\[ L = N(r) \times r \]

or

\[ N(r) = L \times r^{-1} \]

in 2-D:

\[ N(r) = L^2 \times r^{-2} \]

in \( d \)-D:

\[ N(r) = L^d \times r^{-d} \]
Taking log on both sides, one gets

\[ \log (N(r)) = d \times [\log L + \log (1/r)] \]

or

\[ d = \frac{\log (N(r))}{\log L + \log (1/r)} \]  \hspace{1cm} (1.5)

As, \( r \to 0 \) implies that \( \log L + \log (1/r) \sim \log (1/r) \),

Then, \( d \to D \) (fractal dimension)

Therefore,

\[ D = \frac{\log (N(r))}{\log (1/r)} \]  \hspace{1cm} (1.6)

So, the relation between the number of boxes and the magnitude of the box side determines the fractal dimension D according to relation:

\[ N(r) \sim r^{-D} \]  \hspace{1cm} (1.7)

The demonstration of the box counting algorithm is shown in figure 1.5:

Different fractal dimension calculation methods have their individual advantages and disadvantages. A comparison of various methods which have been explained in this section namely Richardson method, mass radius method and box counting method is briefly given below. The routine calculation of fractal dimension using fractal models with image processing technology is often adapted.

Richardson method is suitable for analyzing curves in a planar field and is not suitable for analyzing object involving other objects scattered within an image.

On the other hand, mass radius method is suitable for application of structural analysis but not for textural analysis. Hence, it is not suitable for complex patterns.

The box counting method is applied for textural and structural analysis of a structure. The mesh grid also allows to analyze the fractal dimension of objects involving other objects within an image. This method can be furthermore used to analyze the irregularities in surfaces filling the space volume. In this thesis, we have used the box counting method for calculating the fractal dimension.
1.2.3 Types of fractals

According to Family’s classification [42], fractal objects can be divided into two main types:

- deterministic fractals
- random fractals or statistical fractals

1.2.3.1 Deterministic fractals

Deterministic fractals are generated iteratively in a deterministic way. The deterministic patterns are self similar objects that are precisely consistent on the basis of some basic laws. In other words, the rescaled object $r(A)$ perfectly overlaps a piece
of the original object ‘A’, is called deterministic self similar fractal. Typical examples of such fractals are the Cantor set (dust), the Koch curve, the Sierpinskki carpet. These examples are discussed in section 1.2.4. The two most important properties of deterministic fractals could be said to be:

- precise calculation of fractal dimension
- the indefinite range \((-\infty, +\infty)\) of their self similarity

It is possible to construct infinite number of deterministic fractals with fractal dimension by dividing a line, plane or volume into infinite number of fragments by various means. Few of the fractal geometries are discussed below.

1.2.3.2 Random fractals

Random fractals are generated by random processes. However, natural objects can often be classified as random fractals as natural objects do not contain identical scaled down copies within themselves because the natural structures are truncated at certain scales. The object A is called statistically self similar when \(r(A)\) is not congruent with the subsets \(A_1, A_2, \ldots, A_n\) but is identical in all statistical respects. The most important characteristic of random fractals is the spatial and/or sample-to-sample fluctuation in their properties, e.g., fractal landscapes, percolation clusters (see section 1.2.6), trajectories of Brownian motion and Brownian tree (i.e., fractals generated by modelling diffusion limited aggregation or reaction limited aggregation clusters, see section 1.2.5.3 and 1.2.6).

1.2.4 Fractal geometries

1.2.4.1 Cantor dust

The nineteenth century German mathematician George Cantor became fascinated by the infinite number of points on a line segment. The construction is as follows:

First stage starts with a Euclidean line segment of unit length (containing infinite number of points). In the second step, one third of the length- the middle third- is removed as shown in figure 1.6. This leaves two line segments of length 1/3 each. In the third step, again the middle third of the remaining segment is removed, thus leaving 4 segments, Table 1.2. This procedure of deleting the middle third of each segment is carried out at every stage as shown in figure 1.6. In the limit of an
infinite number of stages, the remaining set of points forms the so called Cantor dust. Dust here refers to topological dimension of zero just as a curve and surface denote sets of topological dimension of 1 and 2, respectively.

In the limit \( n \to \infty \) which is the same as \( r \to 0 \), application of Eq. 1.6 gives the fractal dimension as:

\[
D = \lim_{n \to \infty} \frac{\log 2^n}{\log 3^n}
\]

\[D \approx 0.6309\]  

(1.8)

<table>
<thead>
<tr>
<th>No. of stages</th>
<th>Scale length</th>
<th>No. of segments</th>
<th>Total length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial stage</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1(^{st}) stage</td>
<td>1/3</td>
<td>2</td>
<td>(2 \times (1/3))</td>
</tr>
<tr>
<td>2(^{nd}) stage</td>
<td>((1/3)^2)</td>
<td>(2^2)</td>
<td>(2^2 \times (1/3)^2)</td>
</tr>
<tr>
<td>3(^{rd}) stage</td>
<td>((1/3)^3)</td>
<td>(2^3)</td>
<td>(2^3 \times (1/3)^3)</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>N(^{th}) stage</td>
<td>((1/3)^n)</td>
<td>(2^n)</td>
<td>(2^n \times (1/3)^n)</td>
</tr>
</tbody>
</table>

Table 1.2: Stages of forming Cantor dust

Figure 1.6: Classical construction of Cantor set proceeds by repeatedly removing the middle thirds of all line segments [43]
1.2.4.2 Koch curve

The von Koch curve was first introduced by the Swedish mathematician Helge von Koch. The Koch curve was created to show how to construct a continuous curve that didn’t have any tangent line.

The sequential construction of Koch curve begins with a straight line (A), figure 1.7. Then, the middle third line is raised to produce an equilateral triangle (B). Raising equilateral triangle from the middle third of each of the line segments in the object produces the image (C), Table 1.3. Because of the resolution limits of the printing process, at higher stages of construction (D, E, and so on) the fine details of the complex curve would be lost.

In the limit $n \to \infty$ which is the same as $r \to 0$, application of Eq. 1.6 gives the fractal dimension as:

$$D = \lim_{n \to \infty} \frac{\log 4^n}{\log 3^n}$$

$$D \approx 1.2618$$

<table>
<thead>
<tr>
<th>No. of stages</th>
<th>Scale length</th>
<th>No. of segments</th>
<th>Total length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial stage</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1st stage</td>
<td>1/3</td>
<td>4</td>
<td>$4 \times (1/3)$</td>
</tr>
<tr>
<td>2nd stage</td>
<td>$(1/3)^2$</td>
<td>$4^2$</td>
<td>$4^2 \times (1/3)^2$</td>
</tr>
<tr>
<td>3rd stage</td>
<td>$(1/3)^3$</td>
<td>$4^3$</td>
<td>$4^3 \times (1/3)^3$</td>
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<td>.</td>
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<tr>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Nth stage</td>
<td>$(1/3)^n$</td>
<td>$4^n$</td>
<td>$4^n \times (1/3)^n$</td>
</tr>
</tbody>
</table>
1.2.4.3 Sierpinski gasket

It is also another well known example of geometric fractal. The gasket was named after Waclaw Sierpinski, a polish mathematician who described its main properties in 1916. The construction starts out with a solid triangle (like the Koch curve) and is constructed through recursive pattern. Unlike the Koch curve, the construction removes smaller versions of original triangle instead of adding them to the original (figure 1.8), Table 1.4.

In the limit $n \to \infty$ which is the same as $r \to 0$, application of Eq. 1.6 gives the fractal dimension as:

$$D = \lim_{n \to \infty} \frac{\log 3^n}{\log 2^n}$$

$$D \approx 1.5849$$
Table 1.4: Stages of forming the Sierpinski’s gasket

<table>
<thead>
<tr>
<th>No. of stages</th>
<th>Scale length</th>
<th>No. of units</th>
<th>Total area in units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Stage</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1st stage</td>
<td>1/2</td>
<td>3</td>
<td>3 × (1/2)</td>
</tr>
<tr>
<td>2nd stage</td>
<td>(1/2)^2</td>
<td>3^2</td>
<td>3^3 × (1/2)^3</td>
</tr>
<tr>
<td>3rd stage</td>
<td>(1/2)^3</td>
<td>3^3</td>
<td>3^3 × (1/2)^3</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Nth stage</td>
<td>(1/2)^n</td>
<td>3^n</td>
<td>3^n × (1/2)^n</td>
</tr>
</tbody>
</table>

Figure 1.8: Classical construction of the Sierpinski gasket proceeds by repeatedly removing the middle part of the remaining triangle [33]

1.2.5 Significance of fractals

Fractals infuse our lives, appearing in places as tiny as the membrane of a cell and as majestic as the universe. The concept of fractals has been used in many fields like chemistry, physics, biology, medicine and the stock market, where it helps in understanding the extraordinary pattern formation and chaos. Apart from a theoretical and qualitative description of the observation made in nature, they are
used in game and film industry to produce natural looking landscapes, plants, texture, clouds etc. [40].

1.2.5.1 Fractals in nature

Fractal geometry is used to describe, model and analyse complex forms found in nature. The natural objects occurring as fractals such as clouds, mountains, river networks and plants, cannot be accommodated by Euclidean geometry as natural objects are not of simple structures but are structures which exhibit irregularities and complexities. Plants like trees, ferns, and broccoli are fractal objects found in nature and they can be modelled using simple algorithms. Weather patterns like lightning, clouds, rains, snowflakes also have a fractal pattern [7]. Fractal behaviour is also associated with many geological features like coastlines [44], mountain ranges, seismic faults, craters [45], ocean waves [46], and river networks [47, 48]. Some natural fractals are given in figure 1.9.

![Figure 1.9: Natural fractals: (a) lightning, (b) coastline, (c) broccoli and (d) snowflake [49]](image)
1.2.5.2 Fractals in biological sciences

Biological systems and processes are characterized by many levels of substructures that possess characteristics such as self-similarity, irregularity and length invariance. Branching structure of many biological structures in the human body include regional distribution of pulmonary blood flow, pulmonary alveolar structure, distribution of arthropod body lengths and trabecular bone structure in vertebral specimen [50]. In biology, fractal dimension is possessed by the branched networks of blood and pulmonary vessels in human body [50], time series of heart beat [51], retinal vessels [52] and proteins (transport and diffusion in them) [53]. Figure 1.10 shows the example of naturally occurring fractals in human body. As mentioned in the previous section, fractal objects occurring in nature lack strict self-similarity, which means that in most biological systems, there is a lower limit to self similarity and also the addition of an element of randomness to its fractal structure as depicted in figure 1.10.

Figure 1.10: Naturally occurring fractal in human body: (a) folds on the surface of the brain and (b) branching of blood vessels in human body [54]

1.2.5.3 Fractals in physical sciences

The physics of far from equilibrium growth phenomenon represents one of the important fields where fractal geometry is widely applied. Examples for such processes include the microscopic condensation of gold particles in thin films [55], electro-deposition of ions on to electrodes, crystal morphology [56], viscous fingering which is observed when a viscous fluid is injected into a more viscous one [57, 58] and many other physical systems [46, 59]. In addition to interfacial growth, computer
models based on growing clusters (via aggregation) represent another class of growth phenomenon. Aggregation takes place particle by particle while in other cases, the aggregates themselves are also mobile and join together to form larger clusters during their motion. A detailed overview on aggregation processes is given in section 1.2.6. The following text gives some examples of fractals in physical systems.

1.2.5.3.1 Dielectric breakdown

It is a typical random growth process. It occurs when electric field is strong enough leading to the formation of electrically conducting regions in an insulating material. For instance, intense electric field during thunderstorm which produces conducting path in air along which many electrons flow, is the best known version of this phenomenon. A formal model was proposed by Niemeyer, Pietronero and Weismann in 1984 [5]. They obtained radially symmetric patterns (i.e., conducting phase) by applying strongly inhomogeneous electric field above the breakdown voltage within an insulator to a compressed SF$_6$ gas. Recently, I. Dierking has studied dielectric breakdown patterns of liquid crystal Hele-Shaw cells [60].

The model typically describes the macroscopic behaviour combining diffusion limited aggregation with electric field for solids, liquids and gases.

1.2.5.3.2 Viscous fingering

Viscous fingering is the most widely studied fractal pattern in Hele-Shaw channel where one observes fingering patterns when glycerol is displaced by air [61]. In 1898, Henry Selby Hele-Shaw [56] introduced a simple system to study the flow of water around various objects. He designed Hele-Shaw cells consisting of two parallel transparent plates separated by a relatively small gap. Two immiscible viscous fluids with high viscosity were placed in the narrow gap between the two parallel plates. Pressure was applied either in one of the edge (the linear version, longitudinally) or at center of the upper plate of the cell (the radial version). In the linear version, because of the stabilizing effects of the side walls, steady state fingers can develop in the cell while in case of radial version, growth of disordered interfaces occur. Figure 1.11 shows the principle of a linear and a radial Hele-Shaw cell.
It is notable that DLA is a stochastic version of the Hele-Shaw pattern. In the Hele-Shaw cell, flow in composite fluids with high and low viscosities forms the patterns, the particles diffuse in the DLA, while the fluid pressure diffuses in the Hele-Shaw flow [61]. These are related to each other.

Recently, Luo and Zhang [63] have simulated the viscous fingering occurring in Hele-Shaw cell using modified DLA model.

Figure 1.11: (a) Longitudinal and radial Hele-Shaw cells and (b) typical viscous fingering patterns [62]

1.2.5.3.3 Electrodeposition

Another most extensively studied DLA process is the growth by electrochemical deposition. Several researchers have studied the growth of metallic forms resulting due to electrodeposition of metals on a substrate in a simple electrolytic cell.

In 1984, R. M. Brady and R. C. Ball pointed out black dendritic growth of copper electrodeposition in steady state diffusion limited conditions onto an initially
point like cathode [64]. Fractal behaviour was observed and fractal dimension D was found to be $2.43 \pm 0.03$.

The confirmation of the fractal nature for zinc metal leaves grown by electrodeposition was done by M. Matushita et al. in 1984 [65]. In their experiments, zinc metal leaves were grown two-dimensionally by applying a dc voltage between the carbon cathode and a zinc ring plate anode. Figure 1.12 shows a typical zinc dendrite that was electrodeposited on to the cathode. The fractal dimension D was found to vary with applied dc voltage.

![Fractal structure of zinc metal leaves grown by electrodeposition. Photographs a-d were taken 3, 5, 9 and 15 min after initiating the electrolysis, respectively [65]](image)

Sawada et al. [66] and Grier et al. [67] also studied the fractal patterns during electrodeposition of zinc. Sawada et al. reported electrodeposition of zinc with a different configuration and monitored patterns with electrolyte concentration while Grier et al. reported a transition region between diffusion limited aggregation and dendritic growth which was dependent on the applied voltage. They also reported the occurrence of metastable crystalline form of zinc produced during electrodeposition.
There is also a study of the effect of magnetic field on the electrodeposition of Zinc by Mogi et al. [68]. They found that the growth morphology drastically changed from DLA-like and dendritic patterns from 0T to a spiral pattern and an asymmetric dendrite in magnetic fields lower than 0.5T.

Recently, Suda et al. [69] studied the effect of temperature on the morphology of the growth of two dimensional zinc metal leaves. With increasing temperature, the morphology changed from DLA-like to a disc-like pattern. For temperature lower than 20°C, fractal dimension was found to be 1.66 and with increasing temperature, fractal dimension D increased almost linearly with temperature.

### 1.2.6 Review of fractal aggregation models

Aggregation models produce complicated geometrical objects which represent a theoretical approach to the problem of pattern formation [12, 13]. These models play an important role in understanding far from equilibrium growth processes. For growing fractals, the fractal dimension D can be defined through the linear function \( N(L) \sim L^D \) where, \( L \) is the linear size of the object and \( N(L) \) is number of boxes of unit volume \( L=1 \) that are needed to cover the structure [12].

This section presents some aggregation models to provide information on different possibilities that an aggregation model can offer in the growth processes.

#### 1.2.6.1 Eden model

The Eden model is the simplest growth model and was proposed by Eden in 1961 to simulate the growth of tumors [70]. The algorithm can be summarised as follows: place a seed particle at the origin, for example the center of lattice (i.e., at \( x, y = 0 \)) in figure 1.13. The unoccupied sites that are nearest neighbours to an occupied site are denoted as growth or perimeter site. In simpler version of this model, a perimeter site is chosen at random and a particle is added, rendering it occupied, and thus a cluster site. The process of repeating perimeter site to clusters site is repeated until large clusters of occupied sites are formed. An example of cluster with 1000 particles and its growth is shown in figure 1.13.
The physical justification for Eden model is simple. The bacteria are not supposed to be moving and so the only way for the colony to grow is via offsprings. It is assumed that bacteria will divide itself only if it has sufficient room to do so.

![Eden cluster of 1000 particles](image)

**Figure 1.13: Eden cluster of 1000 particles [71]**

This means that any bacteria which is completely surrounded is basically dead. Every variation of Eden model has a biological justification but the bottom line is that, apart from the restriction just mentioned, division can occur anywhere with equal probability. This model, therefore, doesn’t take into account the conditions in which the bacteria grow. There is no shortage of food and no inhibition of growth by waste produced by other cells.

1.2.6.2 Percolation model

The publication of Broadbent and Hammersley [72] in the year 1957 about their work on flow of liquids in porous media, started the study of percolation theory, a widely studied branch in statistical physics. It has application in modelling of forest fires, diffusion in disordered media and oil fields, etc.
Imagine a fluid poured on top of a porous medium. The fluid spreading through the medium may be of two different types of randomness. One case is random walk of fluid particles and the other case in which randomness is frozen into the medium itself and it is known as the “percolation process”, as it behaves like a coffee in a percolator. The site percolation process as introduced by Broadbent and Hammersley is defined as follows.

Consider the sites of square lattice of size N. Consider each site is occupied with probability p or vacant with probability (1-p), independently of all neighbouring sites on the lattice. For large systems (in terms of number of sites (say N) as well as geometric size) this means that pN sites are occupied, while at two values of p one finds only small clusters as shown in figure 1.14. They grow with increasing p until one cluster spans the system, connecting the top and bottom of the lattice. Figure 1.14 shows the visual representation of a percolation cluster, representing five clusters of mass (the number of occupied sites within a cluster) 1, one of mass 2, two of mass 3 and three of mass 4. The cluster is called spanning cluster. If “percolation probability P(p)” is defined as the probability that origin is a part of an infinite cluster, then, below a certain value p = p_c (critical probability), P(p) is always zero. As p is increased above p_c, the percolation probability becomes non-zero. This change in behaviour is an example of a phase transition as shown in figure 1.15.

[Image: Figure 1.14: Percolation cluster [73]]
1.2.6.3 Diffusion limited aggregation

All the clusters do not grow like the Eden model and the percolation models. As an example, consider the snowflake where the cluster forms by adding particles to the cluster that come from outside and at some point connect with the cluster. Such behaviour is captured by the model called diffusion limited aggregation.

This model provides an example of how random motion can give rise to beautiful self similar clusters. DLA was first proposed by Witten and Sander [74] in 1981 and has since been the starting point for many studies. There is wealth of research on DLA usually in two dimensions. One of the first particle aggregate structures was the simple DLA model described below in detail.

The growth is remarkably simple. In the first step, the seed is fixed at the origin of some co-ordinate system. Another particle is released from far away boundary and the particle undergoes random walk, i.e., diffuses until it arrives at a site adjacent to the seed particle and forms a two particle aggregate. Then, another particle is released and allowed to walk until it reaches a site adjacent to the one of the two particles in the cluster and sticks. The process is repeated many times until a large cluster is formed. Some of the properties of a DLA cluster are:
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- it is non-equilibrium phenomenon
- it is nonlocal process, i.e., the diffusion of particles in space is influenced by distant particles of the system in addition to its immediate neighbour.
- the aggregates are not completely solid objects, they contain voids.
- as the cluster grows, it increasingly becomes more and more compact.
- it has sticking probabilities less than one. In other words, we can say that a new particle sticks to the growing aggregate with a probability $P_s$ and continues to diffuse with a probability $1-P_s$.
- there are next-to-nearest neighbour interactions, i.e., when the particle arrives at a site which is a next neighbour to the aggregate, then it stops.
- there is at present no special theory in order to satisfactorily describe all DLA-related phenomenon. But, with various assumptions, one can solve the laplace equation:

$$\nabla^2 \rho(r) = 0$$

with boundary condition $\rho(r) = 0$ on sites adjacent to the aggregate surface, where, $\rho(r)$ is the probability of finding the particle in a certain site $r$ outside the aggregate.

In the first approximation, DLA can be viewed as self similar fractals. DLA clusters are self similar in a stochastic sense: if we zoom on the branched object of DLA, we will never find the exact same structure again. However, statistical properties are reproduced and parts of a cluster look pretty much alike after a proper rescaling. Figure 1.16 shows cluster of 10000 particles and figure 1.17 shows the image of large 3D DLA aggregate.

Fractal structures via laplacian growth (of which diffusion limited aggregation (DLA) is one of the most common type) can be used to describe many naturally occurring phenomena such as formation of snowflake. Many other studied phenomena include polymer morphology [77, 78], dielectric breakdown [79], viscous fingering [56, 57], instances of biological growth [80, 81], tree structure and the paths of lightning bolts [82].
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1.2.6.4 Cluster-cluster aggregation

The process is called cluster-cluster aggregation (CCA) to distinguish it from particle-cluster aggregation phenomenon as discussed in section 1.2.6.3, that is, DLA in which all the particles that stick to the cluster are of the same size and the cluster that is formed is a single stationary aggregate (motionless). In cluster-cluster aggregation,
clusters themselves are allowed to move around and aggregate with one another. However, to study the structure of aggregates and the dynamics of the formation of CCA, simple computer models have been successfully studied. These kinds of models have a wide variety of applications in physical systems such as; aggregation of aerosols particles, coagulation and gelation in colloids, sedimentation of debris in rivers and the galaxies clusters. The two models of cluster-cluster aggregation on which main attention has been focussed are the cases where the aggregate is diffusion limited or reaction limited.

In diffusion limited cluster aggregation (DLCA) [83, 84], two particles stick rigidly together as soon as they contact and the structure and kinetics are determined purely by Brownian motion of clusters. However, this leads to quite tenuous open structures.

In reaction limited cluster aggregation (RLCA) [85, 86], a small but relevant repulsive potential barrier can prevent clusters from joining each other even if they are close. However, after a number of contacts they may join irreversibly. This leads to rather compact structures.

One of the most realistic models of CCA include particle-cluster and cluster-cluster aggregation in which various aggregation phenomena take place during thin film growth by vapour deposition [87].

1.2.7 Aggregation model in this thesis

**Large size fractals using DLA model**

DLA is one of the most important models of fractal growth. Diffusion limited aggregation model has finite-size of particles which is the very reason of dendrite structures of DLA. This cluster forming procedure is repeated many times and if the number of particles contained in the DLA cluster is huge (typically $10^4$-$10^8$, see figure 1.18), the cluster generated by this process is highly branched and forms fractal structures. Figure 1.19 illustrates the model that represents such a growth. A simulated result for a 2d DLA is shown in figure 1.18. The probability field is quasistationary and in the complement of the cluster we have again $\nabla^2 \rho(r) = 0$. In this case, the boundary condition on the cluster is, $\rho(r) = 0$, but finite time singularities are
avoided by having finite size particles. The boundary condition at infinity is exactly as above. Figure 1.19 gives a visual representation of the above mentioned process.

DLA requires the Brownian motion. Brownian motion occurs when a number of particles are immersed in a fluid and allowed to move freely. If Brownian motion is the dominant form of acceleration for primary particles, this motion can be assumed to also drive particle attachment and aggregate structure formation.

![Figure 1.18: Simulated 2D DLA cluster with 30000 particles [66]](image)

![Figure 1.19: Aggregation using DLA model](image)
1.3 FRACTALS IN POLYMERS

1.3.1 Definition of polymer

The word polymer comes from the Greek word “polymeros” where “poly” refers to “many” and “meros” refer to “parts”. Polymers are long chain molecules, sometimes called macromolecules. They are formed by polymerizing many small molecules called “monomers”. Polymers can be classified as biological and non-biological macromolecules. Furthermore, the non-biological polymers can be classified depending upon the architecture and/or chemical composition of the polymer. Polymers classified by their architecture include linear, grafted or cross-linked polymers while polymers classified by their chemical composition include homopolymers, diblock copolymers, triblock copolymers, random block copolymers and grafted copolymers. Homopolymers consist of one type of monomer and the copolymers consist of different monomers (monomer A, B,...). The block of a polymer is a small homopolymer consisting of m monomers \((A_m)\) sequentially attached whereas block copolymer consists of blocks where each block has been attached to form the polymer. The abbreviations for a diblock copolymer and tri-block copolymer are: \(A_mB_n\) and \(A_mB_nA_m\) where \(m\) and \(n\) are the numbers of monomers of A and B, respectively. Table 1.5 illustrates the differences between polymers w.r.t. their structure and chemical composition.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Composition</th>
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Table 1.5: Non-biological polymers w.r.t. (a) structure and (b) chemical composition
33

Chapters 3, 4 and 5 of this thesis comprise of studies on fractal growth in ion conducting polymer matrix.

1.3.2 Polymer electrolyte

An electrolyte is a substance that contains free ions and usually consists of salt or salts that are dissolved in a medium. Electrolyte is an integral part in many electrochemical devices such as batteries, super capacitors, electrochromic devices etc. Conventionally, electrolytes consist of liquids which may be either caustic or flammable like potassium hydroxide solution in an alkaline battery and sulphuric acid in lead acid battery. Various solid electrolytes have been developed as alternatives to liquid electrolytes. The many advantages of solid electrolytes over liquid electrolytes have motivated intensive research in this area since the past few decades as they result in a leakage-free, corrosion-free, environment friendly and easy to fabricate devices.

One of the class of solid electrolyte is the polymer electrolyte. A polymer electrolyte consists of an inorganic salt dissolved in a polymer host. Conducting polymer-salt complexes were first described in the early 1970’s [88, 89] and were quickly adopted by the electrochemical community which recognized the polymer electrolyte medium for vital applications such as energy, storage and electrochemical displays [90, 91]. Polymer electrolytes can be of the following types [92]:

- Solvent-free polymer-salt system in which ion conduction takes place due to one or several salts in a high or low molecular weight polar polymer matrix.
- Gel polymer electrolytes which are usually obtained by incorporating a larger quantity of liquid plasticizer and/or solvents to a polymer matrix. During gelation, a more viscous polymer solution is converted into a high viscosity system, a stable gel with polymer host structure.
- Plasticized electrolyte, where small amount of high dielectric constant solvent or ionic liquid have been added to conducting polymer-salt system to increase its conductivity. The mixing of plasticizers in the ion conducting polymer electrolyte leads to the decrease in their crystallinity and an increase in the segmental motion of the polymer chains. The mixing may also support ion dissociation which results in a large number of conducting ions for charge transport.
• Ionic rubber which is a low temperature (“low” here is nevertheless above room temperature) molten salt mixture (like chloroaluminates) rubberized by the addition of polymers into a three dimensional network.

• Proton exchange membranes (PEM) used, in particular, in different types of solid polymer electrolyte fuel cells (PEMFC). The most important example of this kind of polymer electrolyte is Naflon [93].

1.3.2.1 PEO based polymer electrolyte

PEO is the most common polymer used so far and forms one of the most extensively studied polymer based ionic conductors because of the suitable structure of PEO in supporting fast ion transport. The polymeric chain of PEO is capable of displaying flexibility and can coordinate to many different cations. A segment of PEO polymer chain is shown in figure 1.20.

![Figure 1.20: A segment of poly (ethylene oxide) chain](image)

1.3.2.1.1 Physical properties of PEO

The melting temperature ($T_m$) and glass transition temperature ($T_g$) of PEO is a function of average molecular weight and the molecular weight distribution of the sample. Usually, $T_m$ varies from 60°C for lower molecular weights (~ 4000 g/mol) to 66°C for higher molecular weight (~100,000 g/mol) [94], and $T_g$ increases from
-65°C for a sample with a molecular weight of ~100,000 g/mol [95] to -17°C by decreasing the molecular weight to 6000 g/mol [96]. PEO is completely soluble in water and is also soluble in a wide range of common organic solvents [97]. The conductivity of PEO is of the order of $10^{-8} \text{ S/cm}$ [98]. The conductivity can be increased to the level of $10^{-4} \text{ S/cm}$ at room temperature by using various conductivity promotion methods.

1.3.2.1.2 Solvation mechanism in PEO

For most polymer/salt-complexes, cations should bind to the polymer chain instead of other ions [92]. For other ions to move freely into the polymer matrix, anions should have minimal interaction with the polymer and the cations. A salt with small univalent cation and a large anion is needed to satisfy all these requirements.

The cation-polymer interactions determine the solubility and ionization of salt in the PEO which can be according to hard/soft acid base (HSAB) principle [92, 94]. The principle was formulated by Pearson in order to predict the solubility of complexes between Lewis acids and bases. The principle states that matching hard acids (smaller and non-polarizable) with hard bases (polarisable ligands with high electronegativity) or soft acids with soft bases yields the strongest interaction/or solvation. For PEO with hard bases, the best candidate for cations are non-polarizable small cations, e.g., Li$^+$ or Na$^+$. A large anion with delocalized charge is needed to dissolve ions in less polar solvents, such as polyether. For polyether based polymer electrolytes, the following order predicts the most appropriate anions [92, 94, 99]:

$$\text{F}^- << \text{Cl}^- < \text{I}^- < \text{AlO}_2^- < \text{ClO}_4^- < \text{CF}_3\text{SO}_3^- < \text{BF}_4^- \sim \text{AsF}_6^-$$

In polymer chains, cations are able to move between coordination sites, either on one chain or between neighbouring chains, called intrachain hopping and interchain hopping, respectively (see figure 1.21). Moreover, considering ion association from the ion-ion interactions between ions, there are other types of hopping mechanisms involving ion clusters, as shown in figure 1.22.
Figure 1.21: Cation motion in a polymer electrolyte assisted by polymer chains only [94]

Figure 1.22: Cation motion in a polymer electrolyte assisted by ionic cluster [94]
1.3.3 Fractals in polymers: An overview

Fractal geometry is a tool that has been widely employed for the study of fractal structure. In polymer science, fractal analysis is useful when studying polymer surfaces and even polymer matrix. However, the emphasis is mainly on the former one as it can reflect some information on the latter one. In polymer science, polymer growth can be considered as a fractal process. Therefore, there is a need to develop new techniques or modify available ones for this purpose.

Much of our understanding about mechanism of forming aggregates or flocs has been mainly due to computer simulations. The first mechanism was carried out by Vold in 1963 [100] who used the ballistic aggregation model and found that the number of particles $N(r)$ within a distance $r$ measured from the first seed particle is given by $N(r) \sim r^{2.3}$. The researches on fractal aggregates have developed simulation models on DLA introduced by T. A. Witten and L. M. Sander in 1981 [74] and on the DLCA model proposed by P. Meakin in 1983 [83] and M. Kolb et al. in 1983 [84], independently. The DLA has been used to describe diverse phenomena forming fractal patterns such as electrodeposition, dielectric breakdown and viscous fingering. These phenomena are briefly discussed earlier in section 1.2.5.3.

The fractal concept seen in complex and irregular objects are also encountered in conducting polymers as these polymers grow randomly during polymerization at microscopic level and aggregate also randomly. The STM and AFM constitute excellent tools for the investigation of the fractal aspect of conducting polymers [101]. This is a subject of numerous studies ranging from basic to applied sciences. Schaefer and Keefer [102] studied fractal geometry of branched silica polymers produced by condensation polymerization. The fractal dimension was measured by small angle X-ray scattering and found to be equal to $2\pm0.1$. Experimental studies of the statics and dynamics of diffusion-controlled polymerization has been done by Kaufman et al. [103]. They reported the preparation of polypyrrole which varied from diffusion-controlled polymerization to diffusion-limited polymerization and observed growth instability as the structure changed continuously from compact to dendritic to that of random aggregate. The fractal dimension was found to be equal to $1.74\pm0.01$. Several complementary studies addressing the fractal growth due to electropolymerization of pyrrole have been done [16, 104, 105].
These studies on conducting polymers throw light on the kinetics and dependence of pattern formation due to polymerization [106] and formation of neuron like pattern and dendrimers in conducting polymers [107].

1.3.3.1 Fractal growth in ion conducting polymeric media

Many experiments have been performed to test the predicted DLA pattern. However, most of the experiments were done by applying some sort of a stimuli (electric field, magnetic field, pressure etc.) which gave very small (μm) size fractal patterns.

- Chandra and coworkers (figure 1.23) chose an ion conducting polymeric system to obtain large size fractals without any external stimuli in the laboratory framework in the PEO:NH₄I (+Al₂O₃) system. They found that:

![Figure 1.23: (a) Computer simulated [59] and (b) experimentally observed [18] fractal patterns](image)

The growth is humidity dependent (i.e., humidity must be >60%). If humidity was < 60% no fractal growth was observed. The high humidity offered slow drying of film and enough time for aggregation to take place. Also, in ion conducting polymer electrolytes, σ is temperature dependent, higher the temperature, higher is the σ (and therefore, higher was the mobility of ions).
ii. The number of nucleation centre depended upon the amount of dispersed Al\(_2\)O\(_3\) and the nucleation centres were more for higher NH\(_4\)^+/EO ratios. They also reported that all nucleation centres did not grow equally.

iii. By fluorescence studies [20], the group showed that the fractal patterns were formed by higher polyiodides (possibly I\(_3^-\)). They reported that pure iodine gave fluorescence peaks at 585nm, 640nm, and 685nm. These peaks were present in all samples. However, the film with extensive fractal growth showed 10nm shift from its original peak position which indicated that there was involvement of higher polyiodide species in fractal growth. Chandra and coworkers predicted the mechanism as follows: the addition of Al\(_2\)O\(_3\) in PEO:NH\(_4\)I knocked out I\(^-\) which hangs from the ether oxygen of PEO chain after complexion. This I\(^-\) first formed an I\(_2\) molecule which then stuck to another I\(^-\) to form I\(_3^-\). The same group also reported that if the humidity was <65%, then aggregation of I\(_2\) took place which gave rise to a “strain field”.

iv. They also reported [19] the growth of universal DLA by providing interface with teflon rings of different radii which confirmed Counder’s [110] computer simulated patterns growing along the periphery of circle with random walkers that were assumed to be emitted from its centre, figure 1.24.

![Figure 1.24](image)

**Figure 1.24** (a) Computer simulated [108] and (b) experimentally observed [19] fractal patterns
v. The group also observed experimentally the theoretically simulated DLA patterns of Irisawa et al. [111]. Figure 1.25 shows the theoretically simulated (left hand side, a-c) and experimentally observed DLA undergoing thermal relaxation (right hand side, d-f).

![Figure 1.25: (a-c) Theoretically simulated DLA [109] and (d-f) experimentally observed pattern after annealing polymeric film with frozen fractal patterns](image)

- Amir et al. [22-25] simulated fractal growth patterns in ion conducting polymer electrolyte (PVDF-HFP/PEMA-NH₄CF₃SO₃-Cr₂O₃, PEO-NH₄I) membranes by developing a model based on Brownian motion. The experimentally grown fractal pattern in PVDF-HFP/PEMA-NH₄CF₃SO₃-Cr₂O₃, PEO-NH₄I membranes are shown in figure 1.26. The same group in another paper studied the fractal growth pattern in PEO and Chitosan.
membranes and simulated the experimentally obtained fractal patterns by using DLA based on Brownian motion theory. They showed that the computer simulated fractal pattern dimension and experimentally obtained fractal pattern dimension was approximately the same. The experimentally cultured fractal pattern growth in PEO and Chitosan membranes by Amir et al. [22-25] are shown in figure 1.27 below.

Figure 1.26: Fractal growth in (a) PVDF-HFP/PEMA-NH$_4$CF$_3$SO$_3$-Cr$_2$O$_3$ and (b) PEO-NH$_4$I membranes

Figure 1.27: (a) DLA patterns in PEO: NH$_4$I (60:40) and (b) fractal in films of Chitosan doped with silver nitrate
1.3.3.3.1 Significance of the work done

Electrochemistry at fractal interfaces [110-116] indicates that batteries can be described as fractal objects [117] since the fractal geometry seems to maximize the surface to area ratio while minimizing the energy lost during transport within the network. The effect of fractal pattern growth phenomenon in secondary battery has not been fully understood. Many researchers [118 and references therein] have made significant contribution towards the understanding of this phenomenon. It is difficult to study the growth of fractal patterns that form at the electrode. Thus, fractal pattern growth in ion conducting polymer electrolyte acts as a laboratory framework for the study and simulation of the conditions of fractal growth. This thesis is a step ahead to understand the mechanism of fractal pattern formation in polymer electrolytes.

1.4 STRUCTURE OF THE THESIS

The structure of the thesis is as follows:

Chapter 1 briefly explains the research background. This chapter gives an overview of fractal theory including the description and characteristics of fractals. Finally, this chapter covers the literature review on fractals in polymers.

Chapter 2 describes the sample preparation methods for growing large size fractals in ion conducting polymer matrix and experimental techniques used such as X-ray diffraction (XRD), Raman spectroscopy and impedance spectroscopy which have been employed to study the fractal growth in polymeric media.

Chapter 3 reports large size fractal growth in a ion conducting polymer electrolyte composites. This chapter examines the aggregating species which lead to fractal patterns via XRD and Raman spectroscopy. The steady state of ion diffusion in polymer electrolyte has been analyzed in the framework of the Nernst-Planck equation. The ion transport mechanism has been studied with the help of ac conductivity.

Chapter 4 describes the influence of electric field on large size fractal growth. Moreover, this observation provides the experimental evidence of theoretical simulations done by Zhi-Jie Tan et al. [Physics Letters A 268 (2000) 112] and Huang
and Hibbert [Physica A 233 (1996) 888]. The growth is governed by diffusion, convection and migration in an electric field which undergoes a transition from random growth to directional growth.

Chapter 5 extends the earlier work of chapter 4 by including the influence of low values of electric field on the DLA in polymer electrolyte composites. Different kinds of electrode geometries have been used to simulate the growth under external field by setting the value of field above the threshold value.

In the final chapter, Chapter 6, the work has been summarized and conclusions drawn from the results described in the previous chapters.

The appendices contain algorithms which have been used to process the raw image file in order to calculate the fractal dimension (Appendix 1), a general overview on polyiodides (Appendix 2) and the Nernst-Planck equation (Appendix 3).
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