The fractals theory and its application to various physical and chemical processes have recently undergone a large amount of development [1–7]. For simplification of understanding of the results represented in subsequent chapters some main notions and definitions are briefly considered and reasons for the application of fractal analysis (and connected with it irreversible aggregation models) for description of the structure and properties of polymer materials and composites on this basis are shown.

2.1 The Fractal Analysis of Polymeric Media

Self-similar objects, invariant about local dilatations, i.e., objects which in observation processes at various magnifications repeat the same form, are called fractals. Mandelbrot [1] introduced the notion of fractals as self-similar sets, defining a fractal as a set for which the Hausdorff–Bezikovich dimension always exceeds the topological dimension. The fractal dimension \( d_f \) of the object, adopted in \( d \)-dimensional Euclidean space, varies from 1 to \( d \). Fractal objects are natural fillings of sets between known Euclideans with whole number dimensions 0, 1, 2, 3, ... The majority of objects existing in nature turn out to be fractal ones, which is the main reason for the vigorous development of fractal analysis methods.

According to Family’s classification [8], fractal objects can be divided into two main types: deterministic and statistical. The deterministic fractals are self-similar objects, which are precisely constructed on the basis of some basic laws. Typical examples of such fractals are the Cantor set (‘dust’), the Koch curve, the Serpinski carpet, the Vichek snowflake and so on. The two most important properties of deterministic fractals are the possibility of precise calculation of their fractal dimension and the unlimited range \((-\infty; +\infty)\) of their self-similarity. Since a line, plane or volume can be divided into an infinite number of fragments by various modes then it is possible to construct an infinite number of deterministic fractals with different fractal dimensions. In this connection the deterministic fractals are impossible to classify without introduction of their other parameters in addition to the fractal dimension.

Statistical fractals are raised by unordered (random) processes. A disorder element is
typical for the majority of physical phenomena and objects. The fact of sufficiency of the fulfilment of the disorder condition for formation of fractals was first noted by Mandelbrot [1]. A statistical walk is a typical example of such a fractal. However, purely statistical models often inadequately describe real physical systems. One cause of this is an excluded volume effect. The essence of this effect consists in a geometrical restriction, forbidding two different system elements to occupy the same space volume. This restriction should be taken into account in corresponding model constructions [9]. The best known examples of such models are walks without self-intersections, ‘lattice animals’ and statistical percolation.

In the range of definite scales fractals have different topological structures depending on the maximum number of elements that are connected with the given system element. If each element can be connected, as a minimum, with two other ones, then the received structure has no branches. By analogy with linear polymers Family [8] calls this type of fractal linear. If branching occurs, then the resulting fractal has a network-like structure; this type of fractal was called a branched fractal.

A polymer’s microstructure can possess a high degree of natural or artificially created self-ordering [10], which is one limiting case. The other limiting case is chaos, as opposed to order. As a rule, such systems were obtained in conditions far from thermodynamical equilibrium; they fill the gap between periodic structures and completely unordered systems [11]. In other words, fractal structures should possess a definite level of intermediate order, therefore in studying thermodynamically non-equilibrium solid media (which, as a rule, polymers are [12]) possessing local order [13], the question about interrelation of structures of local order level and their fractality degree is very important.

At present there can be no doubt about the fact that solid medium approximation cannot serve as an adequate model for real polymers [14]. Just as in the synthesis of polymers a large number of micro-, mezo- and macrodefects appears in them, which can develop in the exploitation process of products from polymers. What is more, it is empirically established that even at initially homogeneous media deformation they acquire hierarchical block structure, characteristic space scales of which $L_i$ satisfy the relationship with a sufficient degree of precision:

$$ \Lambda_i = \frac{L_{i+1}}{L_i} = \text{const} \quad (2.1) $$

where $\Lambda_i$ is the automodelity coefficient; $i = 0, 1, 2, \ldots$ [15, 16].
The Main Physical Concepts used in Fractals Theory

One of the main characteristics of solid body structure features is the Euclidean dimension $d$, which can accept the following values: $d = 0$ – point defects, $d = 1$ – linear defects (dislocations), $d = 2$ – planar defects (grains boundaries, doubles and so on), $d = 3$ – three-dimensional (spatial) formations. The Euclidean dimensions can serve as characteristics of high-ordered symmetrical microstructures, which are not often formed even in the materials obtained in quasi-equilibrium conditions. Non-equilibrium systems, prepared in highly non-equilibrium conditions and presenting themselves as a peculiar replica of dynamic dissipative structures, cannot be described adequately within the frameworks of metal- and X-ray studies in general [15–19]. This is all the more true for solid-like or glassy polymers – thermodynamically non-equilibrium systems by definition. So, the atomic structure of non-equilibrium materials can have quasi-crystalline order possessing symmetry elements of the fifth, seventh, thirteenth and higher orders [19] forbidden by the Brave theorem, lying in the basis of classical methods of X-ray analysis. Moreover numerous fractographic [5, 17, 19] and geophysical [16] studies indicate in many materials structure fractality and the essentially non-Euclidean geometry of the fracture and deformation of solid bodies. By virtue of this traditional solid medium, mechanics methods, based on the strains homogeneity assumption, considered as reflections of deforming body samples in Euclidean space, cannot describe adequately the rheological behaviour and fracture of real materials, in particular polymers displaying such properties as high elasticity and viscoelasticity.

The essential progress in the solution of this problem is connected with synergetics (synergetics is a border field of knowledge, devoted to the general laws revealing the formation, stability and decay processes of ordered temporal and spatial structures in complex non-equilibrium systems of various natures [4]) and fractal analysis ideas and methods using [4, 5, 7, 18, 19]. Specifically, it has been shown that at first sight absolutely unordered chaotic systems, forming in non-equilibrium conditions (amorphous phases, fracture surfaces and so on), display actually ordering peculiar elements [2, 18]. If crystals are characterised by definite symmetry and translational invariance, then non-equilibrium structures can possess enantiomorphism properties [4], even if they do not possess quasi-crystalline structure; these systems are scale-invariant in the definite self-similarity range [1, 2]. The so-called Renie dimensions $d_q$ serve as a self-similarity quantitative characteristic, which, unlike the topological dimension, can have both even and fractional magnitudes [1], determined by the relationships:
Structure and Properties of Crosslinked Polymers

\[
\begin{align*}
  d_q &= \begin{cases} 
    \lim_{\varepsilon \to \infty} \ln \sum_{i=1}^{M} P_i^q(\varepsilon) (1 - q) \ln \varepsilon & q \neq 1 \\
    \lim_{\varepsilon \to \infty} \frac{\ln \sum_{i=1}^{M} P_i(\varepsilon) \ln P_i(\varepsilon)}{\ln \varepsilon} & q = 1 
  \end{cases} 
\end{align*}
\]

(2.2)

where \(M\) is a minimum number of \(d\)-dimensional cubes with the side \(\varepsilon\), necessary for covering all structure elements; \(P_i(\varepsilon)\) is the probability of the event that a structure point belongs to the \(i\)-th volume \(\varepsilon^d\) covering the element; \(q\) is a measure transformation parameter (‘magnification parameter’).

For Euclidean objects (smooth curves, regular lattices on planes and in volumes and so on) the identity is carried out [14]:

\[d_q = d \quad \text{where} \quad -\infty < q < \infty\]  

(2.3)

For regular mathematical fractals of Cantor sets, Koch curves and Serpinski carpets, constructed by recurrent procedures, the Renie dimension \(d_q\) does not depend on \(q\), but on [14]:

\[d_q = d_H = \text{const} < d, \quad -\infty < q < \infty\]  

(2.4)

where \(d_H\) is the Hausdorff–Bezikovich dimension (Hausdorff dimension).

According to the mathematical definition [3], the Hausdorff dimension \(d_H\) is a local characteristic of the set in the chosen scales range, which can be covered with ‘balls’ not necessarily of the same size under the condition that all ‘balls’ diameters are smaller than the chosen diameter. The structure fractal dimension \(d_f\) is a physically determined value within the scale range in which structure elements are self-similar,
The Main Physical Concepts used in Fractals Theory

i.e., they are fractals. Since \( d_f \) and \( d_H \) scale ranges coincide, then \( d_f = d_H \) is called the structure fractal (Hausdorff) dimension.

Natural fractals, such as clouds, polymers, aerogels, porous media, dendrites, cracks, solid fracture surfaces and so on, possess only statistical self-similarity, which takes place only in the restricted range of the spatial scales [1–3, 14]. For solid-like polymers it has been experimentally shown [20] that such a range spreads from several angstroms up to several tens of angstroms.

The interrelation of local order and the fractality degree of disordered solids can be described by common mathematical terms. Specifically, speaking about the structure of solid polymers, one should note that the majority of researchers assume the availability in them of segmental scale structural formations has been proved, although the packing concrete type in these formations remains debatable [13, 21].

One should underline that the notion about an amorphous state being an absolutely disordered one is incorrect. According to the Ramsey theorem [22], any sufficiently large number \( i > R(i, j) \) of points or objects (in the considered case—the structure elements) contains without fail a high-ordered subsystem from \( N_j \leq R(i, j) \) elements. Therefore absolutely disordered systems (structures) do not exist. It has been similarly shown that any structure consisting of \( N \) elements at \( N_j > B_N(j) \) presents itself totally of a finite number \( k \leq j \) of self-similar structures inserted into each other, the Hausdorff dimension of which in the general case can be different. This means that any system independent of physical nature, consisting of a sufficiently large number of elements, is multifractal (in the special case—fractal) and is characterised by Renie dimensions \( d_q \) spectrum, \( q = -\infty \rightarrow \infty \) [23]. The tendency of the condensed systems to self-organisation in scale-invariant multifractal forms is the consequence of the main principles of open systems thermodynamics and \( d_q \) are defined by competition between short- and long-range interatomic interactions, defining bulk compressibility and shearing stiffness of solids, respectively [24].

Another very important property of fractals, distinguishing them from traditional Euclidean objects, is the necessity of at least three dimension determinations: \( d \) — seized Euclidean space dimension, \( d_f \) — fractal (Hausdorff) dimension and \( d_s \) — spectral (fracton) dimension, characterising object connectivity. For Euclidean spaces \( d = d_f = d_s \) and this circumstance allows Euclidean objects to be considered as special (‘degenerated’) cases of fractal objects. We will meet the given rule herein again and again [25]. This means that for fractal objects (for example, polymers) structure description in two fractal dimensions (\( d_f \) and \( d_s \)) is required even at the fixed \( d \) value. Such a situation corresponds to the non-equilibrium thermodynamics rule, according to which for thermodynamically non-equilibrium solids (polymers), for which the Prigogine–Defay criterion is not fulfilled, the description of two order parameters, as a minimum, is necessary [12].
Fractal objects are characterised by the following relationship between mass $M$ (or density $\rho$) and measure linear scale $L$ [23]:

$$M(L) \sim L^{d_m}$$  \hspace{1cm} (2.5)

where $d_m$ is the mass scaling exponent.

Unlike mathematical fractals, real fractals (including polymers) have two natural length scales $L_{\text{min}}$ and $L_{\text{max}}$ (Figure 2.1); objects below and above are not fractal [23]. The lower limit $L_{\text{min}}$ is connected with the finite size of the structural elements and the upper one $L_{\text{max}}$ with uneven aspiration for the limit $d_f$. As was noted above, for polymers it was experimentally stated [20, 26, 27] that $L_{\text{min}}$ has an order of several angstroms and $L_{\text{max}}$ of several tens of angstroms.

![Figure 2.1](image-url)  

*Figure 2.1* The dependence of the density $\rho$ on the linear scale $L$ of a real fractal. The range $L_{\text{min}}$–$L_{\text{max}}$ is the region of object fractal behaviour [23]

In polymer research, situations often occur when strictly derived relationships describe high-elastic media, for example, elastomers, which are usually analysed at
temperatures higher than their glass transition temperature $T_g$, but do not describe the behaviour of polymers, which are in a glassy state. At first it was explained by the sharp reduction in the lower $T_g$ of the molecular mobility of the chains or by structure ‘freezing’ [28]. Strictly speaking, the principal distinction between higher and lower $T_g$ of the molecular structure does exist—in both cases it consists of long-chain macromolecules [29]. The distinction consists in the transition of a polymer from a thermodynamically non-equilibrium state with lower $T_g$ to a quasi-equilibrium state with higher $T$. Within the frameworks of fractal analysis this means that a polymer structure at $T \geq T_g$ ceases to be fractal and becomes a Euclidean body (or, at any rate, approaches it sufficiently closely).

According to [30], an ability to sustain a large deformation with the following complete restoration of characteristics after stress removal is a property that actually all polymers, consisting of long-chain macromolecules, show at corresponding conditions. The given property (stresses relaxation) in one way or another is found beyond temperature range bounds, corresponding to displaying high-elasticity. In other words, a polymer’s macromolecular nature exercises a prevalent influence on its physical properties at deformation, forcing the medium to display such qualities as yielding, high-elasticity and vitreousness. In virtue of this it can be supposed that the same fractal dimension can be used for object description in different physical states [29, 30].

It is known that polymers possess multi-level different scales structure (molecular, topological, supermolecular, floccular or block levels), elements of which are interconnected [7, 43]. As a result of a force on a polymer new (secondary) structural elements can be formed – cracks, fracture surfaces, plastic deformation zones and so on. The indicated different structural elements and also the processes forming them are characterised by heterogeneous parameters, therefore up to now only empirical correlations between them were established. If each of the indicated elements (processes) is characterised by a uniform parameter, for example, by fractal dimension, then analytical relationships connecting them, not containing fitting parameters, can be obtained. It is important for properties and behaviour prediction of high-molecular compounds in exploitation. Let us note that fractal analysis was applied and turned out to be useful in high-elasticity [14, 32] and yielding [22, 33–35] phenomena descriptions.

It is obvious that for the correct use of methods based on fractal dimension estimation it is necessary to apply physically well-founded parameters describing a polymer’s structure. In this sense Euclidean and fractal objects are principally different: for the first only one dimension of space (Euclidean) is required and for fractal objects no fewer than three dimensions [25].
2.2 The Fractal Models of Polymer Medium Structure

The cluster model will be used below in structure analysis of amorphous polymers as a local order model [13, 36, 37]. This model establishes that local order domains (clusters), immersed in a loosely packed matrix, consist of several densely packed collinear segments of different macromolecules, i.e., they are amorphous analogues of a crystallite with drawing chains (CDC). The length of the segments which the cluster consists of is accepted to be equal to a polymer statistical segment length \( l_{st} \). At the same time clusters play a role of multifunctional nodes of physical entanglements network with density \( n_{cl} \). It is accepted in the first approximation that the number of segments in clusters per polymer volume unit is equal to \( n_{cl} \). This assumption allows determination of the relative fraction of clusters \( \varphi_{cl} \) [37].

The main factor that defines interconnection of local order and the fractal nature of the structure of solid polymers is the fact that both these features are a reflection of the key property of these polymers— their thermodynamical non-equilibrium nature. The scales of fractal behaviour \( L_{min} \) and \( L_{max} \) indicated above correspond very well to cluster structure border sizes: \( L_{min} \) to statistical segment length \( l_{st} \), \( L_{max} \) – to distance between clusters \( R_{cl} \) [38].

However, one should not forget that fractal analysis gives only a common mathematic description of a polymer’s structure, i.e., it does not identify those structural units (elements) that any real polymer consists of. The cluster model of polymer amorphous state structure allows one to obtain a physical description of a thermodynamically non-equilibrium polymer’s structure with local (short-range) order representations drawing and molecular characteristics usage, which identifies its element quantitatively. Since these models consider polymer structure from different positions, they are a very good complement of one another [7, 29].

As it is known [39], structures that are fractal on small scales and homogeneous on large scales are called homogeneous fractals. Such fractals are percolation clusters at the percolation threshold. As it was shown in papers [40, 41], the cluster structure is a percolation system and by virtue of the above is a homogeneous fractal. In other words, the availability of local order in polymers, in a condensed state, is defined by their structure fractality.

The structure fractal dimension \( d_f \) can be expressed as follows [39]:

\[
d_f = d - \frac{\beta}{v}
\]  

(2.6)
where b and n are critical indices, the definitions of which were introduced in percolation theory [39].

Hence, the condition $\beta > 0$, which follows from the percolation theory [39] and experimental data for cluster structure of polymers [40, 41], also defines the fractality of the structure of polymers. It is obvious that the indicated condition and, consequently, the fractality of the structure of polymers define the dependence of $\varphi_{cl}$ on the testing temperature, i.e., local order of thermal fluctuation nature. In other words, the structure fractality and local order ‘frozen’ lower than $T_g$ are interexcluded notions.

The rules considered above allow quantitative interconnection of fractal dimension $d_f$ and local order characteristic $\varphi_{cl}$ (or $n_{cl}$) to be obtained. The analytical relationship between indicated parameters has the following form [7]:

$$d_f = d - 6(l_0 \nu_{cl})^{1/2}$$  \hspace{1cm} (2.7)

where $l_0$ is the polymer main chain skeletal bond length. In Equation 2.7 $l_0$ is given in m.

Equation 2.7 gives two forms of analytical relation between $d_f$ and $\varphi_{cl}$ (or $n_{cl}$), the physical grounds for which were considered above. Let us note the important conclusion, following from Equation 2.7. The fractal dimension $d_f$ depends not only on the order parameter value $\varphi_{cl}$, but also on the polymer’s molecular characteristics ($C_{\infty}$ and $S$), where $C_{\infty}$ is the characteristic ratio, which is an indicator of polymer chain statistical flexibility [42], $S$ is a macromolecule cross-sectional area. This is the reflection of the above-mentioned rule, that for description of a polymer’s condensed state structure, as a minimum two order parameters are required [12, 25].

An experimentally proved solid polymers structure fractality serves as another reason in favour of the local order model. As follows from Figure 2.1 data, fractality requires density $\rho$ gradient on definite length scales $L(L_{\text{min}} - L_{\text{max}})$. The cluster model corresponds to this requirement, since the density of clusters is higher than that of the loosely packed matrix, which ensures $\rho$ as a necessary gradient. Flory’s ‘felt’ model [43], which assumes that polymer structure is presented as chaotically tangled statistical coils, denies local order availability. It is obvious that such a model does not force the $\rho$ gradient and, hence, does not correspond to a polymer’s experimentally stated structure fractality.

Therefore, a close interconnection exists between notions of local order and fractality.
in the case of a polymer’s condensed state having fundamental physical grounds and expressed by a simple analytical relation.

2.3 Polymer Medium with Scaling Theory Positions

Researchers of different trends have various scaling notions (scaling invariance). The authors of the present work mainly share de Gennes’ point of view [44], which assumes that it is necessary, as far as it is possible, to distract from the considered system structure details and to select simple universal features, which are typical for a wide class of systems. A scaling law always defines only some asymptotics, the applicability of which, taking into account system specific features, it is necessary to analyse concretely for each case. By his works de Gennes offers a new level of study of a polymer’s structural-physical properties, as Flory had done before [45]. Fractal dimension can serve as a scaling characteristic (scaling index) example, which as has been shown for regular fractals, depends on the system formation mechanism only and defines the global structure of the system, the mass distribution depending on scale.

The universality hypothesis is closely connected with the scaling hypothesis, although if it is to be approached more strictly, they should be considered as independent suppositions [46]. The universality hypothesis essentially states that if the same limiting conditions are typical (system parts interactions) for different mechanisms of the formation of systems, then these systems come to be in one universal class of physical phenomena. Such a class is characterised by a definite set of scaling constants (indices). The fact that universality classes contain not only physical systems (sometimes those that belong to different natural sciences fields) but also theoretical models gives the possibility of simulation and imitation on a wide range of computer applications. It should be noted that the universality of different classes can also have different forms of scaling laws – different types of relations, describing the system and the equations – connecting scaling constants between them [47].

One of the examples of the scaling representation of macromolecules is the ‘reptation’ model [48], according to which the ‘tube’ diameter $\Phi$, in which the macromolecule is confined (equal to the distance between entanglements nodes), can be estimated according to the relationship [49]:

$$\Phi^2 = \bar{N}_\infty \frac{M_{en} l_0^2}{m_0}$$

(2.8)

where $M_{en}$ is the molecular weight of the chain part between entanglements nodes, $m_0$ is the molecular weight of the main chain skeletal bond.
The main distinction between physical entanglements (‘sweeps’) nodes and chemical crosslinking nodes is chains sliding in the former. The density of both can be determined according to the high-elasticity theory and for calculation of chains sliding in entanglements nodes the coefficient 0.8 is added [49].

Another variant of macromolecular chain simulation is considered as a fractal below. In paper [50] it has been noted that with reference to the condensed media the fractal concept is used, but not the observed geometrical image description. As for the macromolecule, simulated by a chain with the fixed valent angles or with the braced internal rotation [42] and consisting of a statistical segment, it is difficult to find a more visual geometrical image for it, than a fractal broken line [29], the more so, such chains self-similarity is strictly proved [51]. It is also necessary to note that macromolecule presentation by both one-dimensional (in a form of a curve line) and three-dimensional (in a form of a cylinder) objects looks like a crude approximation, particularly if its real structure is taken into account – side branching availability, flexible bonds, existence of stiff segments and so on.

For crosslinking epoxy polymers series with varied ratio of hardener reactive groups and epoxy oligomer amounts \( K_{st} \) within the range of 0.5–1.5 chemical crosslinking nodes, the change in density \( v_c \) results in a characteristic extreme change in ratio \( C_\infty \) with a minimum at \( K_{st} = 1.0 \) (the stoichiometric ratio) [52]. To simulate the macromolecule part between chemical crosslinking nodes within the frameworks of the models indicated above [42], then using the known values of this part length \( L_c \) and \( l_{st} \), the typical fractal dependence can be obtained [29]:

\[
N_{st}(l_{st}) = \xi^{-D} N_{st}(1_{st}), \quad \xi < 1
\]  

(2.9)

where \( N_{st} \) is the number of statistical segments per macromolecule fragment with molecular weight \( M_s \), \( \xi \) is the similarity parameter, \( D \) is the fractal dimension of a chain part between chemical crosslinking nodes.

At the conditions \( L_c = \text{const.} \) and \( K_{st} = 1.0, \xi = 0.85 \) was obtained; at \( L_c = \text{const.} \) and \( K_{st} > 1.0, \xi = (0.85)^{1/2} = 0.926 \) was found. Estimation of dimension \( D \) gave the value 1.17. Hence, at the condition indicated above, the fulfilment macromolecule part between chemical crosslinking nodes can be presented as a fractal [29]. With variation in \( K_{st} \) the crosslinking density \( v_c \) changes and, as a consequence, \( L_c \) also changes. This results in the fact that the chain is not quite a self-similar fractal. Nevertheless, it can be simulated by a heterogeneous fractal with the same fragmentation step, but with variable \( D \) value, determined according to the known Richardson equation [23]:
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\[
\frac{L_c}{l_{st}} = \frac{R_c}{l_{st}}^D
\]  

(2.10)

where \( R_c \) is the distance between crosslinking nodes.

The values calculated by the indicated mode \( D \) are listed in Table 2.1:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( K_{st} )</th>
<th>( D )</th>
<th>( C_\infty )</th>
<th>( C_\infty )</th>
<th>( C_\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Data of paper [52]</td>
<td>Calculation according to Equation 2.8</td>
<td>Calculation according to Equation 2.14</td>
</tr>
<tr>
<td>EP-1</td>
<td>0.50</td>
<td>2.06</td>
<td>5.23</td>
<td>4.83</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>1.60</td>
<td>4.32</td>
<td>6.97</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.25</td>
<td>3.38</td>
<td>9.94</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.35</td>
<td>3.75</td>
<td>8.89</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>1.50</td>
<td>4.05</td>
<td>7.68</td>
<td>3.34</td>
</tr>
<tr>
<td>EP-2</td>
<td>0.50</td>
<td>1.85</td>
<td>5.27</td>
<td>6.54</td>
<td>5.35</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>1.43</td>
<td>3.98</td>
<td>8.89</td>
<td>4.69</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.32</td>
<td>3.40</td>
<td>9.24</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.35</td>
<td>3.70</td>
<td>9.24</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>1.55</td>
<td>4.10</td>
<td>7.96</td>
<td>4.29</td>
</tr>
</tbody>
</table>

The results of calculation of the characteristic ratio \( C_\infty \) according to Equation 2.8 do not qualitatively correspond to the paper [52] data: at \( K_{st} = 1.0 \) the value of \( C_\infty \) is a maximum, not a minimum. Since:

\[
\Phi^2 \sim \nu_c^{-2/3}, \ M_c \sim \nu_c^{-1}
\]  

(2.11)
The Main Physical Concepts used in Fractals Theory

then, according to Equation 2.8, the $C_\infty$ value should be proportional to $\nu_c^{1/2}$. In other words, an increase in the density of crosslinking nodes should result in chain flexibility enhancement that does not correspond to the extreme growth of epoxy polymers glass transition temperature [52, 53]. Let us consider the causes of the mentioned disparity. Since:

$$\frac{M_c l_0}{m_0} = L_c$$  \hspace{1cm} (2.12)

then, multiplying and dividing Equation 2.8 on $l_s^2$ we will obtain the relationship [7]:

$$\frac{L_c}{l_s} = \frac{R_c^2}{l_s}$$  \hspace{1cm} (2.13)

which is similar to Equation 2.10. Comparison of Equations 2.10 and 2.13 shows that the scaling relationship in Equation 2.8 is a particular case of the fractal formula in Equation 2.10 with $D = 2$. For the considered epoxy polymers the condition $D = 2$ is not fulfilled (see Table 2.1) and this can be a cause of the found disparity. Using the relationship between Equations 2.8, 2.10 and 2.13 one can write the relationship in Equation 2.8 in a more common form [7]:

$$\Phi^D = C_\infty^{D-1} \frac{M_c l_0^D}{m_0}, \quad 1 < D \leq 2$$  \hspace{1cm} (2.14)

Calculations of $C_\infty$ according to Equation 2.14 give values that correspond well to the data in paper [52]. For a linear polymer the macromolecular entanglements (‘sweeps’) network, the density of which $v_e$ is determined at $T > T_g$ [49], is an analogue of the chemical bonds network.

Therefore, the relationship found in Equation 2.8 is a particular case of a more common fractal relationship in Equation 2.14 and is applicable only to rubbers, for which it was actually derived [29].
2.4 The Fractal Analysis in Molecular Mobility Description Questions

Special attention is always paid to the questions of estimation of molecular mobility of polymer chains [54–56]. The reasons are obvious: thermodynamically non-equilibrium solid-like media, particularly relaxation media, and their physical properties are defined by passing relaxation molecular processes in them, which in turn depend on features of the chemical constitution of the molecular chains and the structural organisation of the polymers [56]. As for parameters, there exist different points of view in describing these processes. So, for example, it is assumed that fast relaxations are defined by the mobility of free chains placed between densely packed domains, which are at the same time nodes of macromolecules physical entanglements network. Such treatment corresponds to the main postulates of the cluster model of the structure of polymers in the amorphous state [13], with the aid of which structure elements can be quantitatively described.

Let us note one more important aspect. The treatment of the structure of amorphous polymers adduced above belongs to elastomers [56]. Transference of these notions on amorphous glassy polymers assumes the description of densely packed domains ‘freezing’, i.e., a sharp increase in their life time. In addition, fractal forms of macromolecules (statistical macromolecular coils), formed in non-equilibrium physical-chemical processes, are preserved (‘frozen’) in polymers. This assumes that in a glassy state the mobility of chain parts between their fixation points will be the main factor defining molecular mobility [57].

The fractal dimension $D$ in paper [57] is chosen as a structural indicator, characterising molecular mobility level for the following reasons. Firstly, between its fixation points the molecular chain part possesses the self-similarity property and has a different dimension from its topological dimension, i.e., a fractal by definition [51]. Secondly, it has been shown [58] that the $D$ value with the variation range of $1 < D \leq 2$ characterises precisely the molecular mobility of the chain part in loosely packed regions [56]. The condition $D=1$ supposes that this chain part loses its fractal nature and mobility loss. Within the frameworks of relaxation spectroscopy this means $\tan \delta = 0$, where $\tan \delta$ is the tangent angle of the mechanical (dielectric) losses. The condition $D = 2$ supposes the maximum possible mobility of the chain part, corresponding to a high-elastic state of the polymer, i.e., it corresponds to maximum value $\tan \delta$ at glass transition temperature $T_g$ [29].

In Figure 2.2 the dependence of $\tan \delta$ on $D$ for the number of copolymers at a measurement frequency of 1 kc [57] is presented. The dependence has clearly defined limits. For $D=1$ it extrapolates to $\tan \delta = 0$. At $D=2$ the $\tan \delta$ value is approximately equal to the corresponding value at $T_g$. Thus, linear dependences with indicated
limiting values \( \tan \delta \) can be used for prediction of fractal dimension [29].

Let us demonstrate the examples of dimension \( D \) usage for the applied problems settlement. The limiting draw ratio \( \lambda_{\text{lim}} \) of polymer tension within the framework of high-elasticity theory is determined according to the formula [59]:

\[
\lambda_{\text{lim}} = n_{st}^{1/2}
\]  

(2.15)

where \( n_{st} \) is the number of statistical segments between entanglements nodes.

This equation was applied repeatedly to glassy polymers as well. In paper [60] the following fractal relationship was obtained:

\[
\lambda_{\text{lim}} = n_{st}^{D/4}
\]  

(2.16)

![Figure 2.2](image.png)

**Figure 2.2** The dependence of the dielectric losses angle tangent \( \tan \delta \) on the fractal dimension \( D \) of the macromolecule part between entanglements for copolyethersulfoneformale with formal blocks contents: (1) 0; (2) 5; (3) 10; (4) 30; (5) 50; and (6) 70 mol\%. The measurement frequency is equal to 1 kc [57]
It is easy to see that an increase in $D$ at $n_{st} = \text{const}$ results in deformability growth of the polymers. **Equations 2.15 and 2.16** are identical at $D = 2$.

The important distinction of **Equations 2.15** and **2.16** is the fact that $\lambda_{im}$ depends on one parameter in the first equation, which is typical for equilibrium Euclidean objects, and in the second on two parameters, which is typical for thermodynamically non-equilibrium fractal objects, therefore **Equation 2.15** using the latter is incorrect.

In paper [61] the relationship between chain statistical flexibility, characterised by $C_\infty$, and dimension $D$ was defined:

$$D = 2 - \frac{1}{C_\infty} \quad \text{(2.17)}$$

Using the literature data for $C_\infty$ [13, 62, 63] the lengths of chain parts between entanglements $L_e$ were calculated. The calculation results correspond to the experimental data (Table 2.2) [29].

Therefore, within the frameworks of fractal analysis an increase in network density with reduction in chain statistical flexibility was obtained. The increase in the number of topological fixation points of macromolecules in the glassy state in comparison with the high-elastic state can be predicted by using fractal analysis methods [29, 61].

The fractal dimension $D$ of the chain part between its topological fixation points (entanglements, clusters, crosslinking nodes) is the most important structural parameter, checking molecular mobility and deformability of polymers. Two of the main factors, due to application of dimension $D$, are its clearly defined variation limits ($1 < D \leq 2$) and the dependence on polymer supersegmental (supermolecular) structure. Let us especially note that all fractal relationships contain, at any rate, two variables.

The obligatory use of, as a minimum, two parameters (for example, $d_s$ and $d_f$ at fixed $d$) is the key condition, following from fractality of macromolecular networks of glassy (solid-like) polymers [29].
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Table 2.2 The values of characteristic ratio $C_\gamma$ and chain part length $L_e$ between entanglements [29]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$C_\gamma$</th>
<th>$L_e$, nm</th>
<th>Experimental</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly $n$-dodecyl methacrylate</td>
<td>13.4</td>
<td>226</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td>Poly $n$-octyl methacrylate</td>
<td>10</td>
<td>177</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>10</td>
<td>104</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl acetate</td>
<td>9.4</td>
<td>88</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>Poly $n$-butyl methacrylate</td>
<td>9.1</td>
<td>130</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Poly methyl methacrylate</td>
<td>8.6</td>
<td>97</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>6.8</td>
<td>56</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>6.7</td>
<td>31</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Poly tetrafluoroethylene</td>
<td>6.3</td>
<td>41</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Polyamide-6</td>
<td>5.3</td>
<td>46</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>Polypropylene oxide</td>
<td>5.1</td>
<td>60</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>4.2</td>
<td>45</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>4.2</td>
<td>21</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Polyester terephthalate</td>
<td>3.3</td>
<td>28</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>2.4</td>
<td>29</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

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