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Fractal analysis of macromolecules

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Abstract. Data on the fractal forms of macromolecules, the existence of which is predetermined by thermodynamic nonequilibrium and by the presence of deterministic order, are considered. The limitations of the concept of polymer fractal (macromolecular coil), of the Vilgis concept, and of the possibility of modelling in terms of the percolation theory and diffusion-limited irreversible aggregation are discussed. It is noted that not only macromolecular coils but also the segments of macromolecules between topological fixing points (cross-links, entanglements) are stochastic fractals; this is confirmed by the model of structure formation in a network polymer. The bibliography includes 141 references.

I. Introduction

The theory of fractals and its application to physical and chemical processes has been vigorously developing in recent years.[1–8] To facilitate the understanding of the results presented in this review, we shall introduce some notions and definitions and consider briefly the grounds for applying the principles of synergetics and fractal analysis to the description of structures and properties of polymers.

Fractals are self-similar objects invariant with respect to local dilatations, *i.e.* objects that reproduce the same shape during observation at various magnifications. The concept of fractals as self-similar ensembles was introduced by Mandelbrot,[1] who defined a fractal as a set for which the Hausdorff – Besicovitch dimension always exceeds the topological dimension. The fractal dimension D of an object inserted in a d-dimensional Euclidean space varies from 1 to d. Fractal objects are the natural filling of the gap between known Euclidean objects with integer dimensions 0, 1, 2, 3... The majority of naturally existing objects proved to be fractal, which is the main reason for the vigorous development of the methods of fractal analysis.

According to the Family classification,[9] fractal objects can be divided into two main types, namely, deterministic and statistical objects. Deterministic fractals are self-similar objects which can be precisely constructed on the basis of several fundamental laws. Typical examples of these fractals are the Cantor set ('dust'), the Koch curve, the Sierpinski gasket, the Vicsek snowflake, *etc*. Two properties of deterministic fractals are most important, namely, the possibility of exact calculation of the fractal dimension and the infinite range of self-similarity ($-\infty$; $+\infty$). Since a line, a plane, or a volume can be divided into an infinite number of fragments in different ways, it is possible to construct an infinite number of deterministic fractals with different fractal dimensions. Therefore, deterministic fractals cannot be classified without introducing other parameters, apart from the fractal dimension.

Statistical fractals are generated by disordered (random) processes. An element of disorder is typical of most real physical phenomena and objects. The fact that disorder, *i.e*. the absence of any spatial correlation, is a sufficient condition for the formation of fractals was first noted by Mandelbrot.[1] A typical example of this type of fractal is the random-walk path. However, real physical systems are often inadequately described by purely statistical models. Among other reasons, this is due to the effect of excluded volume. The essence of this effect lies in the geometric restriction which forbids two different elements of a system to occupy the same volume in space. This restriction is to be taken into account in the corresponding modelling.[10,11] The best-known examples of this type of models are self-avoiding random walk, 'lattice animals' and statistical percolation.

In a definite range of scales, fractals have different topological structures depending on the maximum number of elements connected with the given element of the system. If each element can be connected to not more than two other elements, the resulting structure has no branching. By analogy with linear polymers, Family[9] has called these types of fractals linear fractals. If branching does occur, the resulting fractal has a framework structure; these types of fractals are referred to as branched fractals.

The microstructure of polymers can possess a high degree of self-ordering of either natural or artificial origin;[12] this represents one extreme case. The other extreme case is represented by chaos, which is the antithesis of order. Fractal analysis considers intermediate situations, *i.e*. those located between full order and full chaos. As a rule, these systems are obtained under conditions far from thermodynamic equilibrium; they fill the gap between periodic structures and fully disordered systems.[13] In other words, fractal structures should possess a certain level of intermediate order. Therefore, when studying thermodynamically nonequilibrium solids (the class to which polymers normally belong[14]) possessing a local order,[15] it is important to consider the relationship between the level of local order and the degree of fractality.

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At present, it is beyond doubt that the approximation of a real polymer by a continuous medium is inadequate.[16] Even during the synthesis of polymers, numerous micro-, meso- and macro-defects arise; during performance, they can be further developed. Moreover, it has been found empirically that even those media that are initially homogeneous acquire upon deformation a hierarchical block structure, the characteristic dimensions of which L_i obey, with rather high accuracy, the relation

$$\Lambda_i = \frac{L_{i+1}}{L_i} = \text{const},$$

where Λ_i is the automodelling coefficient, $i = 0, 1, 2, \ldots$ [3, 17, 18]

An important characteristic of structural elements of a solid is Euclidean dimension d, which can take on the following values: $d = 0$ implies point defects, $d = 1$ corresponds to linear defects (dislocations), $d = 2$ means planar defects (grain boundaries, twins, *etc.*), and $d = 3$ describes three-dimensional structures. The Euclidean dimension can characterise highly ordered symmetrical microstructures which do not often arise even in materials produced under quasi-equilibrium conditions. Nonequilibrium systems produced under essentially nonequilibrium conditions, which represent a sort of casts of dynamic dissipative structures, cannot at all be adequately described in terms of classical methods of metallography or radiography.[17–21] This is even more so for solid (vitreous) polymers, which are, by definition, thermodynamically nonequilibrium systems. Indeed, the atomic structure of nonequilibrium materials can possess a quasicrystalline order, characterised by five-, seven-, thirteen- or higher-fold elements of symmetry [21] forbidden by the Brouwer theorem, which underlies the classical techniques of X-ray diffraction analysis. Moreover, numerous fractographical [4, 17, 21] and geophysical [18] studies have revealed fractality of the structures of many materials and essentially non-Euclidean geometry of the deformation and the fracture of solids. Therefore, the traditional methods of the mechanics of continua, which are based on the assumption of homeomorphism of deformations, regarded as imaging of the body being deformed to the Euclidean space, are unable to describe adequately the rheological behaviour and fracture of real materials, in particular, polymers.

A significant breakthrough in tackling this problem is associated with the introduction into physicochemical analysis practice of the ideas and methods of synergetics † and fractal analysis.[3, 5, 6, 8, 20, 21] In particular, it was shown that chaotic systems (amorphous phases, fractured surfaces, *etc.*) formed under nonequilibrium conditions which are totally disordered at first glance, actually display unusual elements of order.[2, 20] Whereas crystals possess a certain symmetry and translational invariance, nonequilibrium systems can possess chirality even if they have no quasicrystalline structure [3] and, what is the most important, these systems are scale invariant in a definite range of self-similarity.[2, 3] Self-similarity is characterised quantitatively by the so-called Renyi dimension d_q. Unlike the topological dimension, it can be both an integer and a fraction [1] and is defined by the relations

$$d_q = \begin{cases} \lim\limits_{\varepsilon \to \infty} \left[\dfrac{\ln \sum_{i=1}^{M} \mathrm{P}_i^q(\varepsilon)}{(1-q)\ln\varepsilon} \right], & q \neq 1, \\ \lim\limits_{\varepsilon \to \infty} \left[\dfrac{\ln \sum_{i=1}^{M} \mathrm{P}_i(\varepsilon) \ln \mathrm{P}_i(\varepsilon)}{\ln\varepsilon} \right], & q = 1, \end{cases}$$

where M is the minimum number of d-meric boxes with side ε needed to cover all the elements of a structure, $\mathrm{P}_i(\varepsilon)$ is the probability that a point of the structure belongs to an ith element of the bulk coverage ε^d, and q is the parameter of transformation of the measure ('magnification parameter').

For Euclidean objects (smooth curves or regular lattices in a plane or in a bulk, *etc.*), the following identity holds:[16]

$$d_q \equiv d, \text{ where } -\infty < q < \infty.$$

In the case of regular mathematical fractals such as the Cantor set, the Koch curves and Sierpinski gaskets constructed by recurrent procedures, the Renyi dimension d_q does not depend on q but[16]

$$d_q = d_{\mathrm{H}} = \text{const} < d, \quad -\infty < q < \infty,$$

where d_{H} is the Hausdorff–Besicovitch dimension (Hausdorff dimension). According to the mathematical definition,[4] the Hausdorff dimension d_{H} is a local characteristic of a set in the range of scales chosen, which can be covered by 'spheres' not necessarily having identical diameters, provided that the diameter of each sphere is smaller than a chosen diameter. The fractal dimension of the structure of a macromolecule d_{f} can be determined physically in the range of scales in which the structure elements are self-similar, *i.e.* when they are fractals. Since the ranges of d_{f} and d_{H} coincide, the $d_{\mathrm{f}} = d_{\mathrm{H}}$ is referred to as the fractal (Hausdorff) dimension of a macromolecule.

Natural fractals such as clouds, polymers, aerogels, porous media, dendrites, colloidal aggregates, cracks, fractured surfaces of solids, *etc.*, possess only statistical self-similarity, which, furthermore, takes place only in a restricted range of sizes in space.[1–4, 16] It has been shown experimentally for solid polymers [22] that this range is from several angstroms to several tens of angstroms.

The relationship between the level of local order and the degree of fractality of disordered solids can be described using general mathematical terms.[3] In particular, as regards the structure of solid polymers, it is noteworthy that the majority of researchers take for granted that segment-size structural associates are formed in polymers, although the particular type of packing in these associates is still debated.[15, 23] It should be emphasised that the view on the amorphous state as being totally disordered is incorrect. According to the Ramsay theorem,[3] any rather great number $i > R(i,j)$ of points or objects (in this particular case, structural elements) contain necessarily a highly ordered subsystem of $N_j \leqslant R(i,j)$ elements. Thus, no totally disordered systems (structures) exist. It can be shown in a similar way that any structure consisting of N elements, where $N_j > B_N(j)$, is a set comprising a finite number $k \leqslant j$ of self-similar structures embedded into one another and having, in the general case, different Hausdorff dimensions. This means that, irrespective of its physical nature, any system consisting of a relatively great number of elements is a multifractal (in a special case, monofractal) characterised by a spectrum of Renyi dimensions d_q, $q = -\infty$ to ∞.[3] The tendency of condensed systems to self-organisation into scale invariant multifractal forms is a consequence of fundamental principles of thermodynamics of open systems and d_q values are determined by the competition between short- and long-range interatomic interactions, which stipulate the volume compressibility and the shear rigidity of solids, respectively.[24] Since the physicochemical properties of polymers depend appreciably on the topology of the structure, the real polymer structures can be studied using the results of physical and mechanical measurements.[25, 26]

Yet another important property of fractals which distinguishes them from traditional Euclidean objects is that at least three dimensions have to be determined, namely, d, the dimension of the enveloping Euclidean space, d_{f}, the fractal (Hausdorff) dimension, and d_{s}, the spectral (fracton) dimension, which characterises the object connectivity. [For Euclidean spaces, $d = d_{\mathrm{f}} = d_{\mathrm{s}}$; this allows Euclidean objects to be regarded as a specific ('degenerate') case of fractal objects. Below we shall repeatedly encounter this statement.][27] This means that two

† Synergetics is an interdisciplinary field of knowledge dealing with identification of the general features of the processes of formation, stability and destruction of ordered time and space patterns in complex nonequilibrium systems of diverse natures.

fractal dimensions, d_f and d_s, are needed to describe the structure of a fractal object (for example, a polymer) even when the d value is fixed. This situation corresponds to the statement of non-equilibrium thermodynamics according to which at least two parameters of order are required to describe thermodynamically nonequilibrium solids (polymers), for which the Prigogine – Defay criterion is not met.[28, 29]

In conclusion, we consider the relationship between the characteristics of percolation and fractal clusters. First of all, note that a percolation cluster near the percolation threshold is a fractal with a dimension of ~ 2.5 (for $d = 3$).[7, 30, 31] This value can be easily derived from the known relationship between d and the critical percolation indices β and ν.[9, 30] The relationships between the critical percolation indices β, ν and t and fractal dimension of a percolation cluster d_f have been reported [7]

$$\beta = \frac{1}{d_f}, \nu = \frac{2}{d_f}, t = \frac{4}{d_f}.$$

The critical indices estimated from these relations fall into the admissible ranges of variation — $\beta = 0.39 - 0.40$, $\nu = 0.8 - 0.9$, and $t = 1.6 - 1.8$, determined in terms of the percolation model for three-dimensional systems. The researchers [7] noted that not only numerical values but also the meanings of these values coincide. Thus the index β characterises the chain structure of a percolation cluster. The $1/d_f$ value, which serves as the index of the first subset of the fractal percolation cluster in the model considered,[7] also determines the chain structure of the cluster. The index ν is related to the cellular texture of the percolation cluster. The $2/d_f$ index of the second subset of the fractal percolation cluster is also associated with the cellular structure. By analogy, the index t defines the large-cellular skeleton of the fractal percolation cluster.‡ Thus, these critical indices are universal and significant for analysis of complex systems, the behaviour of which can be interpreted in terms of the percolation theory.

It has been noted above that the structures and properties of polymers are studied using the principles of synergetics and methods of fractal analysis. This is based on several prerequisites. Firstly, amorphous glassy polymers have thermodynamically nonequilibrium structure.[32] Schäfer and Keefer (see Ref. 10, p. 62) showed that fractal structures are formed in nonequilibrium processes. Therefore, there is good reason to believe that there are fractal structures in glassy polymers and that they can be described using the methods of synergetics. These assumptions have been repeatedly confirmed by experiments.[32 – 39]

For example, the low-frequency region of the spectra of inelastic light scattering of amorphous polymers is a broad structurless plateau.[22] This is due to the fractal structure of polymers on small linear scales.[22, 35]

Fractal objects are characterised by the following relation between the mass M (or density ρ) and the linear scale of measurement L:[3]

$$M(L) \propto L^{d_m}, \quad (1)$$

where d_m is the mass scaling index.

Unlike mathematical fractals, real fractals (including polymers) have two natural scale lengths, L_{min} and L_{max} (Fig. 1); for lengths outside this range, the object is not a fractal.[3] The lower limit L_{min} is related to the finite size of structural elements, while the upper limit L_{max} is associated with the tending to the limit of d_f. It has been found experimentally for polymers [22, 35, 40] that L_{min} has an order of several angstroms and L_{max} is about several tens of angstroms. It is noteworthy that the same range of existence of a local order is typical of the cluster model in which the size (length)

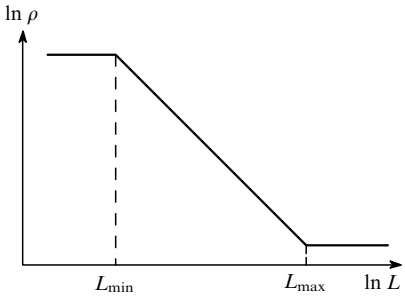


Figure 1. Density ρ *vs.* the length scale L of the real fractal. The range $L_{min} - L_{max}$ is the region of existence of the fractal.[3]

of a statistic segment l_{st} is the lower limit and the distance between the clusters R_{cl} is the upper limit.

It often turns out in studies of polymers that strictly derived relations describe adequately the behaviour of rubbers (*i.e.*, polymers at temperatures above the glass transition temperature T_g) but do not hold for the vitreous state. This is explained, first of all, by the sharp decrease in the mobility of chains below T_g or by 'freezing' of the structure.[41] Strictly speaking, there is no fundamental difference between the molecular structure above and below T_g; in both cases, the structure is formed by long-chain macromolecules. They differ in the fact that the thermodynamically unstable state of the polymer existing below T_g is replaced by a quasi-equilibrium state above T_g. Within the framework of fractal analysis, this means that the polymer structure ceases to be a fractal at $T \geqslant T_g$ and becomes Euclidean body (or, at least, a fairly close approximation). As noted by Flory,[42] the ability to withstand severe deformations and restore entirely the initial characteristics when the stress has been relieved is a property exhibited, under appropriate conditions, by almost any polymer consisting of long-chain macromolecules. This feature is also manifested to some degree beyond the temperature range in which the 'rubber elasticity' phenomenon is observed. In other words, the macromolecular 'essence' of the polymer is more significant than the state in which the polymer occurs. Therefore, the use of the real (fractal) dimension of the object in the relations derived for rubbers [42] is expected to provide fairly accurate results when applied to vitreous polymers.

Secondly, polymers are known to possess multilevel structures (molecular, topological, supermolecular, and floccular or block levels), the elements of which are interconnected.[42, 43] In addition, an external action on a polymer can induce the formation of new (secondary) structural elements — cracks, fractured surfaces, plastic flow regions, *etc*. These primary and secondary structural elements as well as the processes forming them are characterised by miscellaneous parameters; therefore, only empirical correlations have been obtained, at best, between these parameters. If each of the above-mentioned elements (processes) is described by a standard parameter, for example, fractal dimension, one can derive analytical equations relating them to one another and containing no adjustable parameters. This is very significant for the computer synthesis of structure and for the prediction of properties and behaviour of polymeric materials during performance. Note that fractal analysis has been employed successfully to describe the phenomena of rubber elasticity [16, 44, 45] and fluidity.[25, 46 – 48]

Thirdly, legitimate application of these methods requires the use of a physically justified number of parameters describing the polymer structure. In this sense, the Euclidean and fractal objects are fundamentally different: the former require only one space dimension (Euclidean), whereas fractal objects (spaces) require not less than three dimensions.

Yet another important aspect is the change in the fractal dimension of polymers when they are simulated on fractal rather than Euclidean lattices. This fact is also important from the

‡ The relationship between the critical percolation indices and the fractal dimension of the percolation cluster for three-dimensional systems and examples of determination of these values for filled polymers are considered in more detail in the book cited.[7]

practical standpoint for multicomponent polymer systems. The introduction of a dispersed filler into a polymer matrix results in structure 'perturbation'; in terms of fractal analysis, this is expressed as an increase in the fractal dimension of this structure. As shown by Novikov *et al.*,[25] the particles of a dispersed filler form in the polymer matrix a skeleton which possesses fractal (in the general case, multifractal) properties and has a fractal dimension. Thus, the formation of the structure of the polymer matrix in a filled polymer takes place in a fractal rather than Euclidean space; this accounts for the structure modifications of the polymer matrix in composites.

Proceeding from general statements, note that the term 'multifractal' can be understood in two ways as applied to polymers. It is shown below that the fractal dimension of a chain section between points of chemical cross-linking (or between physical entanglements) D is determined by the molecular mass of this section M_s (M_{en}) or by the cross-linking density ν_s (or density of the entanglement network ν_{en}). The M_s (M_{en}) value has a definite distribution;[27] hence, the dimension D would be characterised by a similar distribution.[49] Since the parameter D is uniquely related to the fractal dimension d_f of the supermolecular structure, d_f would be also characterised by a certain distribution. In other words, we are dealing with the distribution of fractal dimensions or multifractals. In addition, all the primary and secondary structural elements mentioned above are also multifractals; therefore, a polymer can be represented as a combination of elements having different weights, *i.e.*, again as a multifractal. Below we shall use averaged values of only the fractal dimensions of particular elements, at least as long as this approximation is useful for the understanding of the physical essence of the problem in question but does not decrease substantially the accuracy of estimates. Thus, the purpose of this review is to describe systematically the results obtained within the framework of fractal formalism and concerned with the studies of structure and properties of polymer macromolecules (linear, cross-linked, amorphous, *etc.*).

II. Modelling of macromolecules

1. Fractal dimension

The complexity of the polymer structure is reflected in the large number of dimensions needed to describe it. Alexander and Orbach [28] proposed the use of spectral or fracton dimension d_s for the description of the density of states on a fractal. The necessity of introducing d_s is due to the fact that the fractal dimension defined by Eqn (1) does not reflect this parameter. The investigators made use of the fact that anomalous diffusion of particles is expected on a fractal and, hence,

$$\langle r^2(t)\rangle \propto t^{2/(2+\delta)}, \tag{2}$$

where $r(t)$ is the distance covered by a diffusing particle in time t and δ is a scaling index for the diffusion constant. Having omitted the intermediate calculations, we present the final result obtained by Song and Roe [14]

$$d_s = \frac{2d_f}{2+\delta}. \tag{3}$$

The spectral dimension d_s is a true property of a fractal and is determined only by its connectivity. It differs from the mass scaling index [see Eqn (1)] or fractal dimension d_f and from the scaling index of the diffusion constant δ by the fact that it does not depend on the way in which a fractal has been inserted into the Euclidean space with dimension d. The dependence of d_s and δ on d_f is described by Eqn (3).

Alexander and Orbach [28] found that for a separate linear polymer chain, $d_s = 1$. In the case of a critical percolation cluster, the d_s value does not depend on d and amounts to $\sim 4/3$ (Table 1).

The dimensions of a linear macromolecule in different states have been considered.[50] The following states are known [50–53] to be the most typical: *1* — compact globule, *2* — coil at the Θ-point, *3* — impermeable coil in a good solvent, *4* — permeable coil (the state typical of rigid-chain macromolecules), *5* — completely uncoiled rod-like macromolecule.

Table 1. Values of d, d_s, d_f and δ for percolation clusters.[28]

d	d_s	d_f	δ
2	1.36	1.9	0.80
3	1.42	2.5	1.55
4	1.39	3.3	2.71
5	1.44	3.8	3.30
∞	4/3	4.0	4.00

The radius of gyration of a macromolecule R_g depends on the molecular mass M and on the geometry of distribution of the molecule in space and is characterised by the scaling index ν (see Refs 32, 50).

$$R_g \propto M^{\nu} \tag{4}$$

From Eqns (1) and (4), it follows that [25]

$$d_f = \frac{1}{\nu}. \tag{5}$$

Baranov *et al.*[50] introduced the dimension d_F, determined from the Flory formula [51] for good solvents

$$d_F = \frac{3-2\nu_F}{\nu_F}. \tag{6}$$

The d_F value reflects the dimension of the sublattice in which the macromolecule is arranged, *i.e.*, it is a fractal dimension of the medium in which the molecule is located rather than of the molecule itself; d_F does not always coincide with the Euclidean dimension. The ν, d_f and d_F values of the three-dimensional space and the states of the macromolecule considered above are listed in Table 2.[52] State *1* is encountered in globular proteins or on precipitation (below the Θ-point) of linear macromolecules from highly dilute solutions.[53, 54] Conformation *5* is typical of some proteins or linear chains exposed to particular types of external action; conformations *2–4* are more trivial and fairly well studied.[51] Analysis of the data of Table 2 leads to the conclusion that, for example, a macromolecular coil in the most frequently encountered states *2–4* is always a fractal (at $d = 3$).

Table 2. Values of ν, d_f, d_F (for $d = 3$) for various states of a macromolecule.[50]

No.	State of macromolecule	ν	d_f	d_F
Poor solvent				
1	Globule	1/3	3	–
2	Coil at the Θ-point	1/2	2	–
Good solvent				
3	Coil	3/5	5/3	3
4	Permeable coil	2/3	3/2	2.5
5	Uncoiled chain	1	1	1

2. Polymer fractal

Cates [55] introduced the notion 'polymer fractal' by replacing the rigid bonds in a percolation cluster by flexible (phantom) links. This model can be used to describe the gelation process (Fig. 2).[56] Within the framework of this approach, Cates [55] described variations of the structure and the dynamics of dilute solutions of polymers. This approach is based on the following main ideas.

The replacement of rigid bonds in a percolation cluster by long phantom chains does not change the connectivity of a fractal (therefore, additional contacts between chains are regarded as

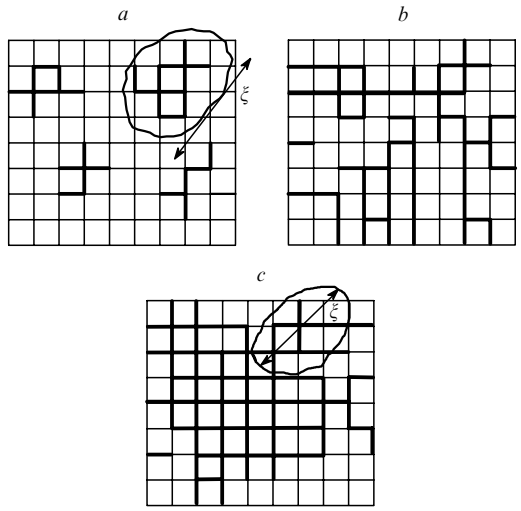


Figure 2. Scheme of the percolation of bonds during gelation:[56] (*a*) pre-gel state, (*b*) gelation point, (*c*) post-gel state; ξ is the characteristic linear scale.

imaginary) but does influence the dimension and the dynamic properties of the object. To describe the changes, at least three fractal dimensions are required.[28] The dimension of the initial fractal (in the percolation lattice) is determined by the fractal dimension d_{f0} using a mass scaling relation similar to (1).[57] The subscript 0 corresponds to the initial fractal with rigid bonds.[55] The dynamic properties can be studied using the spectral dimension d_s or (which is equivalent) using random walkers (the dimension d_w) arranged on a fractal. The latter version implies a scaling law for the root-mean-square displacement r [see Eqn (2)] of a random walker on a fractal in a time t [56]

$$r^{d_{w0}} \propto t, \tag{7}$$

where d_{w0} is the random-walk dimension at $d = 2$.

The case where $d_{w0} = 2$ corresponds to the classical Einstein diffusion. The r value is expressed in Euclidean distances; the process with $d_{w0} > 2$ is usually referred to as slow anomalous diffusion. The density of states is determined by the dimension d_s

$$d_s = \frac{2d_{f0}}{d_{w0}}. \tag{8}$$

It has been noted above that d_s is a true parameter of a fractal determined completely by the object connectivity. The replacement of rigid bonds by flexible links in a percolation cluster does not change d_s, *i.e.* in the Cates procedure,[55] d_s is an invariant value. However, the fractal dimension d_f and the walk dimension d_w change upon execution of this procedure. By using the 'Einstein correlation' relating the scaling indices of a fractal (in this case, d_f is used as the index) to the resistivity (a component of viscosity) $\bar{\xi}$, it can be shown [55, 58] that for polymers with phantom bonds (*i.e.* for polymers with no excluded volume, for which $\bar{\xi} = 2$) the d_w value can be represented by the sum

$$d_w = d_f + 2. \tag{9}$$

Cates showed [55] that relation (9) is also valid for structures containing loops. In the case of an ideal polymer fractal with Gaussian chains and the connectivity parameter d_l, the fractal dimension d_f of a percolation cluster with phantom bonds can be expressed as follows:

$$d_f = \frac{2d_l}{2 - d_l}. \tag{9a}$$

For $d_l = 1$ (linear chains), Eqn (9a) provides the correct value, $d_f = 2$, corresponding to a macromolecular coil at the Θ-point (see Table 2). As noted above, $d_s = 4/3$ for a percolation cluster irrespective of the dimension of the Euclidean space (see Table 1); therefore, from Eqn (9a), we obtain $d_f = 4$, which is consistent with the Flory–Stockmayer theory [59] for phantom chains. For three-dimensional space, $d_f > 3$ has no physical meaning because the object cannot be packed more densely than an object having Euclidean dimension. It is evident that this discrepancy is due to the phantom nature of the polymer chains postulated by Cates;[55] it is necessary to take into account self-interactions of chains due to which the dimension of a polymer fractal assumes a value which has a physical meaning.

In Eqn (9a), d_f has the same meaning as the fractal dimension of phantom Gaussian chains; therefore, the standard mean-field theory, taking account of the factor of excluded volume, can be applied to a polymer fractal.[56]

The Flory approach can be used as the first approximation for this purpose.[59] In this case, the free energy F of an object with self-interactions can be represented by the sum [52]

$$F = \left(\frac{R}{R_0}\right)^2 + v_u \frac{M^2}{R^d}, \tag{10}$$

where R is the size of a real fractal, R_0 is the size of an ideal phantom fractal without allowance for the interactions of excluded volume, v_u is an excluded volume parameter, M is the total mass of the fractal ($R_0^D \propto M$), and d is the dimension of the Euclidean space in which the fractal has been inserted. The first term in Eqn (10) is the elastic (or entropic) component of the free energy and the second term takes into account the volume interactions in terms of the mean-field theory.[52, 59]

By minimising the free energy with respect to R, one can find the fractal dimension D of a swollen fractal, which is determined by the equation

$$D = \frac{d_s(d+2)}{d_s + 2}. \tag{10a}$$

In the case of percolation clusters, Eqn (10a) gives $D = 2$ for $d_s = 4/3$ and $d = 3$ (see Ref. 56), while for linear polymers, $D = 5/3$ for $d_s = 1$ and $d = 3$ (see Ref. 60), which corresponds to an impermeable coil in a good solvent (see Table 2, state *3*). The resulting dimensions are typical of macromolecular coils in monomeric solvents. Using the concept of polymer fractal, one can answer the question of what would happen if the monomeric solvent is replaced by a polymeric one, *i.e.*, whether the polymer clusters and the clusters of a high-molecular-mass 'solvent' would be separated from one another or 'entangled'. This question can be answered by virtue of the equation [60]

$$N = R_g^{D_1 + D_2 - d}, \tag{10b}$$

where N is the number of intersections of two arbitrary fractals with dimensions D_1 and D_2.

The final relations for the dimensions of systems involving mixtures of polymer fractals (fractals in low- and high-molecular-mass solvents, melts of identical and arbitrary fractals) are given in Table 3.[60]

The problems of penetration of polymers with arbitrary connectivity into confined spaces (for examples, pores or slits) have been discussed.[61] It has been noted that the Flory theory, the blob model [61] and the scaling concept provide identical results for linear chains; however, in the case of branched polymers, the Flory theory and scaling can lead to contradictory results when applied without invoking additional information.

For branched (and, hence, for cross-linked) polymers, the equation for the index v in relation (4) has the form [61]

$$v = \frac{d_s + 2}{d + 2}, \tag{11}$$

and the fractal dimension D is determined by the ratio

$$D = \frac{d_s}{v}. \tag{12}$$

Table 3. Final relations for the dimensions of systems comprising mixtures of polymer fractals.[60]

Parameter	Monomeric-solvent $\delta_s=\delta_f=0$	Polymeric solvent $\delta_s=1$, $d_f=2$	Melt of identical fractals $\delta_s=d_s$, $\delta_f=d_f$	Melt of arbitrary fractals
Fractal dimension				
in terms of d_s	$\frac{d_s(d+2)}{d_s+2}$	$\frac{d+2}{2}$	$\frac{d_s(d+2)}{2}$	$\frac{d_s(d+1)(2-\delta_s)}{2(2+d_s-2)}$
in terms of d_f	$\frac{d+2}{2(1+1/d_f)}$	$\frac{d+2}{2}$	$\frac{d+2}{2+1/d_f}$	$\frac{d+2}{2-(\delta_f-2)/d_f}$
Saturation condition [a]	–	$d\leqslant 2$	$d_s\geqslant\frac{2d}{d+2}$	$\delta_f\geqslant 2+\frac{d_f(d-1)}{d}$

Note. The δ_s and δ_f values are the spectral and fractal dimensions of the interglobular space in a solvent.
[a] Transition from fractal to non-fractal behaviour.

Equation (5) is a special case of Eqn (12) for linear chains ($d_s = 1$).

In order to avoid the use of values such as the connectivity parameter (or chemical dimension) d_l or spectral dimension d_s, Lhuillier[62] proposed a d-independent universal index r in the dependence

$$R_{g\,max} \propto N_m^r\,, \tag{13}$$

where $R_{g\,max}$ is the maximum radius of gyration of a macromolecular coil and N_m is the number of base units (monomers) in the chain.

The r value is supposed to vary in the range $1/d \leqslant r \leqslant 1$. It is believed that the r-fractals thus introduced provide a simple description for real polymers: $r = 1$ for linear chains and $r = 3/4$ for branched chains. However, Vilgis[63] have found that, in essence, the following relation holds:

$$r^{-1} = d_s\,; \tag{14}$$

this, in turn, implies that r-fractals can be reduced to polymer fractals, postulated by Cates.[55]

A study by Stepleton *et al.*[64] was among the first which confirmed experimentally the fractal nature of a polymer chain taking a protein as an example. In a study of a frozen aqueous solution of a hemoprotein by electron spin relaxation, its fractal dimension was estimated to be 1.65 ± 0.004. In the opinion of the researchers, this value is in good agreement with the fractal dimension of a self-avoiding random walk, which is equal to 5/3.[57] This conclusion was drawn using the equation for the phonon density of states $\rho(\omega)$

$$\rho(\omega) \propto \omega^{d_s-1},$$

where ω is frequency.

It has been suggested[64,65] that the exponent in the equation for $\rho(\omega)$ is determined by the fractal dimension. However, Alexander and Orbach[28] showed that in this case, the spectral dimension d_s is involved, which is not equal to d_f [see Eqn (8) and Table 1]. Note that the publication by Stepleton *et al.*[64] appeared earlier than the study by Alexander and Orbach.[28] In the case of self-avoiding random walk, $d_s = 1$; substitution of this value into the equation for $\rho(\omega)$ gives a result which, as shown by Young (see Ref. 10, p. 168), is at variance with experimental results.

Attempts to resolve this contradiction have been undertaken.[66,67] Maritan and Stella (see Ref. 10, p. 151) calculated the fractal dimensions for 50 proteins using two methods. In one method, fractal dimension is a scaling index for the contour length of a macromolecule with respect to the distance between its ends (it is equal to 1.19 – 1.82), while in the other method, the fractal dimension is a scaling index for the total mass with respect to the length, which is equal to 1.62 – 2.24. The calculations were performed using X-ray diffraction crystallographic parameters of proteins.

In our opinion, the results obtained for proteins[64,65] do not appear contradictory. Undoubtedly, the fractal dimension presented in the study[64] is the spectral dimension d_s. Its value ($d_s = 1.65$) does not seem too great either, if one takes into account that the values $d_s = 1.65 – 1.80$ were obtained for block poly(-methyl methacrylate).[35] These large values of spectral dimension can be due to several reasons, first of all, to the high connectivity of the polymer chain.[28]

In addition, the polymer chain cannot be modelled by self-avoiding random walk, as has been done by Young. Finally, Cappelli *et al.* (see Ref. 10, p. 156) demonstrated that the effective d_s value can be influenced by the non-homogeneity of block specimens, for example, porosity or inter-grain boundaries.

The difference between the d_l and d_f values found by Colvin and Stepleton[65] can also be easily explained. Indeed, d_l is a chemical dimension, as follows from the way of its determination,[27] d_f is the Hausdorff dimension. These values do not necessarily coincide. By using Eqn (10a) for a fractal swollen in a monomeric solvent, we obtain $D \approx 2.26$ for $d_s = 1.65$ and $d = 3$, which is in good agreement with both experimental data and the limiting D value for branched polymers.[9]

The following relation has been proposed:[62]

$$d_l = \frac{d_f}{z}\,, \tag{15}$$

where

$$z = \frac{4+3D}{8}\,, \text{ for } 4/3 < D < 4. \tag{16}$$

When $D \approx 2.26$, the parameters z and d_l are 1.348 and 1.68, respectively, which is consistent with the estimate made by Colvin and Stepleton.[65] Calculation by an equation similar to (8) gives $d_w \simeq 2.74$, *i.e.* slow anomalous diffusion on the fractal takes place.[28,56]

The following expression relating d_w to d_l has been proposed:[31]

$$d_w = d_f\left(1+\frac{1}{d_l}\right). \tag{17}$$

Assuming that $d_w = 3.37$ ('lattice animals'[31]), we obtain $d_l = 0.93 – 1.98$. This interval agrees with the range of d_l found experimentally.[65]

Thus, there are no contradictions suggested by Young between the estimates made in the two studies cited above[64,65] but the large number of fractal dimensions used to describe the polymer structure creates certain difficulties. This is not a matter of principle because the dimensions considered above are interrelated.[28,55,56,60–63,68–71]

3. Statistical fractal

Family[9] considered the conformations of statistical branched fractals (which simulate branched polymers) formed in equilibrium processes in terms of the Flory theory. Using this approach, he found only three different states of statistical fractals, which were called uncoiled, compensated, and collapsed states. In particular, it was found that in thermally induced phase transitions, clusters occur in the compensated state and have nearly equal fractal dimensions ($\sim$2.5). Recall that the value $d_f = 2.5$ in polymers corresponds to the gelation point; this allows gelation to be classified as a critical phenomenon.

The fractal dimension of purely statistical models, *i.e.* models without the effect of excluded volume, can be determined accurately [see Eqn (9a)]. For linear polymers, this model corresponds to phantom random walk. In the case of branched statistical fractals, the corresponding model is a statistical branched cluster,

whose branching obeys the random-walk statistics. Since the root-mean-square distance between the random-walk ends is proportional to the number of walk steps N, then $D = 2$ irrespective of the space dimension. These types of structures have been studied.[60, 72–74] The value $D = 4$ irrespective of d was obtained for a branched fractal. Unlike 'ideal' statistical models, models with excluded volume, *i.e.* those involving correlations, cannot be accurately solved in the general case. The D_f values for these systems are usually found either using numerical methods such as the Monte Carlo method or taking into account the spatial position of a re-normalisation group.

What are the physical conditions under which a statistical fractal has the most branched structure? It is clear that, when a large number of clusters are present in the system, they all occupy the available volume. The presence of other clusters restricts the degree of branching of each cluster; a cluster is more branched in the isolated state than in a concentrated solution. For polymer coils, this is expressed as an increase in D from its value in a dilute solution in a good solvent to the value at the Θ-point in concentrated solutions.[70]

Yet another factor which also influences the shape of the cluster is whether or not attractive interactions are present. As the temperature increases, the attractive interactions diminish. For example, no interactions of this sort are found in isolated macromolecular coils in good solvents at high temperatures.[74] Family [9] defined this state of a statistical fractal as an uncoiled state because in this case, it is characterised by the smallest fractal dimension.

Then Family used the version of the Flory theory proposed by Isaacson and Lubensky [75] for determination of the fractal dimension of an isolated statistical cluster. The method is based on the determination of the most probable cluster conformation using the free energy of repulsion. Under the influence of elastic free energy, the radius of the real cluster 'tends' to the radius of the ideal cluster which involves no repulsive interaction. After minimisation of the total free energy, the D_f value for an uncoiled cluster can be found from the expression

$$D = \frac{2(d+2)}{5}, \tag{18}$$

which was first obtained by Isaacson and Lubensky [75] for branched polymers in dilute solutions.

Equation (18) has two peculiar features: firstly, D depends appreciably on d and, secondly, there exists a critical dimension of Euclidean space $d_c = 8$ for which $D = 4$ in accordance with the ideal statistical model, *i.e.* the model without correlations. At $d_c > 8$, the correlations caused by the effect of excluded volume are no longer significant and D_f does not change. The value $d_c = 8$ was found in studies of branched polymers and 'lattice animals'.[76] Calculations by formula (18) are in good agreement with the known results for 'lattice animals.'

To elucidate the effects which increase D, Family considered conformations of one big cluster comprising N particles in the presence of other clusters with a size distribution. The large cluster does not 'feel' the presence of other clusters as long as their average diameter is small compared to its diameter. On the scale of lengths much greater than the radius of an average cluster, the big cluster interacts only with clusters similar to itself. It was found for polymers that, as the sizes of other clusters increase, they start to screen the effect of excluded volume, which is effective in the big cluster. The screening can change the fractal dimension of this cluster.

The best examples of processes with a cluster distribution are percolation and thermal critical phenomena, which are reflected, for example, by the Ising, Potts, and other models. Under equilibrium conditions in a system consisting of clusters with a size distribution, the average cluster size deviates in the vicinity of the critical point.

The state of a statistical fractal in which the excluded volume effect is compensated by the screening effect is referred to as the compensated state. For this state, Family has found that

$$D = \frac{d+2}{2}. \tag{19}$$

This expression is expected to be valid for any statistical critical cluster in the presence of clusters having a size distribution. The upper critical dimension for critical clusters can be determined assuming that in Eqn (19), $D = 4$. The result thus obtained, $d_c = 6$, is in good agreement with the data for percolation.[75]

The above results confirm that the presence of numerous clusters and the deviation of the mean cluster size near the critical point results in the screening of the critical volume effect and in an increase in D. Another way of decreasing the repulsive interactions is to enhance the attractive interactions between the elements of an isolated cluster. In the general form, the free repulsive energy can be represented as a power series with respect to density with virial coefficients w_2, w_3, ..., which describe the effects of interaction between pairs, triplets, *etc*.[77] The first term (with w_2) in this power series predominates. However, in the presence of attractive interactions, the second virial coefficient w_2 tends to zero and the term with w_3 should be taken into account. When $w_2 \to 0$, the polymer occurs in the vicinity of the Θ-point.[74] In this case, with minimisation of the total free energy with respect to R

$$D = \frac{4(d+1)}{7}. \tag{20}$$

This relation was first obtained by Bantle [78] for the conformation of an isolated branched polymer at the Θ-point. Calculation in terms of Eqn (20) for $D = 4$ gives $d_c = 6$, as for the compensated state.

Thus, the fractal dimension D increases near the compensation point; this is due either to the geometric screening of the excluded volume effect or to the enhancement of the attractive interaction. Big clusters near the critical point in thermally induced phase transitions and polymers at the Θ-point are examples of statistical fractals in the compensated state.[9]

Study of the conformation of a statistical fractal in a system occurring below the critical point and in the isolated state at $w_2 < 0$ showed that the fractal is very compact and has a globular conformation in both cases. This state of a fractal was called collapsed, by analogy with the collapsed state of polymers.

The conformation of clusters under these conditions was determined using the approach proposed [77] for studying the conformation of a branched polymer in a monodisperse melt, *i.e.* in a solution of coils with identical sizes. In the case of minimisation of the free energy with respect to R,

$$D = d \tag{21}$$

For a purely statistical fractal for which $D = 4$, we obtain $d_{st} = 4$. This means that this type of statistical cluster is compact up to $d = 4$. Therefore, Family [9] called this state of statistical fractals the collapsed state.

In the case of an isolated fractal, attractive interactions predominate below the compensation point; the second virial coefficient w_2 is negative and cannot be neglected in the power series mentioned above. The conformation of a fractal is determined by the balance between the first two terms in this series. The results are identical to Eqn (21) for $d_{st} = 4$. Thus, the conformation of an isolated statistical fractal below the compensation point is the same as the conformation of a big cluster below the critical point.

4. Experimental determination of fractal dimensions

Let us consider several experimental estimates of various fractal dimensions for polymers with allowance for the above theoretical statements. The index ν in Eqn (4) has been determined by small-angle neutron scattering for epoxy polymers;[78] it was found that

$v = 0.6$. It has been suggested [79] that so great a v value is due to the enhanced chain rigidity of epoxy polymers. However, the use of Eqn (11) with $d_s = 4/3$ and $d = 3$ gives $v = 0.666$, which is close to the experimental v value (see Table 2, the permeable coil model). Calculation using Eqn (12) for $d_s = 4/3$ and $v = 0.6$ gives $D \approx 2.22$, which is close to the fractal dimension for the compensated state of branched polymers in accordance with Eqn (20).

Silicate gels and epoxy polymers have been studied by Raman light scattering.[34, 79] The spectral dimension d_s of silicate gels falls within the range from 1.11 to 1.43, depending on the method of calculation, which is consistent with the conclusion drawn by Alexander and Orbach.[28] The results of estimates of d_s from the data of Raman scattering and small-angle neutron scattering for two epoxy polymers with cross-linking densities differing by a factor of two and for the monomer used to prepare these epoxy polymers are presented in Table 4. Attention is drawn to the fact that the d_s values for all the three specimens are virtually equal [if the inaccuracy of determination of d_s is taken to be ± 0.05 (see Ref. 35)], the slight difference being due rather to the determination method used.

Table 4. Value of d_s for the DGEBA monomer [a] and for epoxy polymers based on it determined by Raman light scattering (I) and small-angle neutron scattering (II) methods.[79]

Example	I	II
DGEBA EDA [b] 1X	1.37	1.44
DGEBA EDA [b] 2X	1.33	1.44
DGEBA	1.32	1.52

[a] Diglycidyl ester of bisphenol A. [b] Ethylenediamine.

The results of investigation of the transfer of energy between molecules acting as electron density donors and acceptors have been reported.[80, 81] The Raman scattering method gives actually the fractal dimension of the surface on which the energy transfer takes place.[81] The fractal dimensions found for silicates are in the range of 2.23 – 2.82;[81] that for a polystyrene film is 2.2.[80]

Cappelli *et al*. (see Ref. 10, p. 156) have studied the annihilation of the triplet excitons in naphthalene aggregates located in the pores of various materials including polymers. A common feature of these systems is non-classical annihilation kinetics, which resemble the annihilation kinetics of fractals. The coefficient of the annihilation rate k_a varies with time t

$$k_a \propto t^{-h}, \tag{22}$$

where h is the non-homogeneity index ($0 < h < 1$), which is equal to zero only for homogeneous specimens. The effective spectral dimension of the medium d'_s is given by the relation [70]

$$d'_s = 2(1 - h). \tag{23}$$

The d'_s values for several polymers are listed in Table 5.

Cappelli *et al*.[10] also measured h as a function of temperature. At low temperatures, all the studied polymers exhibit properties similar to the properties of fractals. As the temperature increases, h decreases, *i.e*. the d'_s value increases. In some specimens, $h \to 0$ as the temperature is raised. This implies that all the effects described by fractional dimensions are associated with disorder.[82] A number of specimens behave as fractals also at room temperature. It is noteworthy that the d'_s values for the polymers studied vary over wide limits, from 0.8 to 1.8. In the case of poly(methyl methacrylate), d'_s exactly corresponds to the spectral dimension determined by Raman scattering measurements;[22, 34] it is ~ 1.8 in both cases.

Table 5. Effective spectral dimensions d'_s for some polymers.[10]

Polymer	Pore size μm	T/ K	h	d'_s
Acetate A8	0.2	4	0.16	1.2 – 1.7
Acetate A1	0.1	4	0.47	0.8 – 1.1
Acetate A3	1.2	4	0.44	0.9 – 1.1
Nylon B214	0.2	4	0.21	1.2 – 1.6
Poly(methyl methacrylate)	–	77	0.1	1.8

The theoretical concepts outlined above are confirmed rather accurately by experimental data. Nevertheless, it is worth noting that the concept of polymeric (macromolecular) fractal [55] has been developed for polymer solutions, while the Vilgis theory [60, 61] is applicable only to rubbers and polymer melts, although it has been developed for condensed media. Therefore, it can be expected that extension of these concepts to the vitreous state of polymers would require some corrections taking into account the specific features of this state.

Some possible approximations have been considered by Cates,[55] who concentrated attention on macromolecular entanglements, which play an important role in the description of the behaviour of block polymers.[83 – 86] Cates believes that the fact that the concept of polymer fractal neglects the effects of macromolecular entanglements is the main drawback of this theory. Nevertheless, Cates [55] introduced several simplifications which make it possible to ignore these effects for dilute solutions and relatively low molecular masses. However, in the opinion of Cates, even in the case of predominant influence of entanglements, theoretical interpretation of this phenomenon is impossible without preliminary investigation of the properties of the system in terms of Rouse – Zimm dynamics, which can serve as the basis for a more complex theory. It was assumed [55] that the effects of entanglement can be due to the substantially enhanced local friction of macromolecules.

5. Levels of fractality

Polymers exhibit the fractality inherent in them at different structural levels; both primary and secondary structural elements can be fractals. For example, macromolecular coils in Θ or in good solvents with $d_f \approx 1.66$ (with the Euclidean dimension $d = 3$) are fractals.[1, 29] The fractality of a polymer at the molecular level can be demonstrated as follows. Lebedev [87] reported data on the change in the radius of gyration R_g of the macromolecules of block polystyrene, poly(methyl methacrylate) and polyethylene with the molecular mass M_w. The R_g value is related to the length of a macromolecule L_w in the following way:[88]

$$L_w \propto R_g^{d_f}. \tag{24}$$

The length of a macromolecule can be determined from the known M_w, the molecular mass of one unit m_0, and the projection of the bond length l_0 on the macromolecular axis using the simple dependence

$$L_w = \frac{M_w l_0}{m_0}. \tag{25}$$

The m_0 and l_0 values for the polymers mentioned above were taken from Ref. 89 and Ref. 90, respectively.

Figure 3 *a* shows the variation of L_w *vs*. R_g. Taking account of this dependence, it was found that $d_f \simeq 1.60$, which is close to the corresponding value for a macromolecular coil in a Θ-solvent ($d_f \approx 1.66$, see Table 2). The elements of Koch figures (Fig. 3 *b*) resemble most closely the freely jointed chain model, which is normally used to simulate macromolecules.[91] For this version, $d_f = 1.61$. Thus, the fractality of a block polymer at a molecular level can be regarded as proven.

The cluster model of the structure of amorphous polymers (Fig. 4) provides a quantitative description of supermolecular (supersegmental) structures in this type of polymer. The cluster with chains protruding from it ('interpenetrating' molecules) assumed in this model resembles the well-known cluster used in

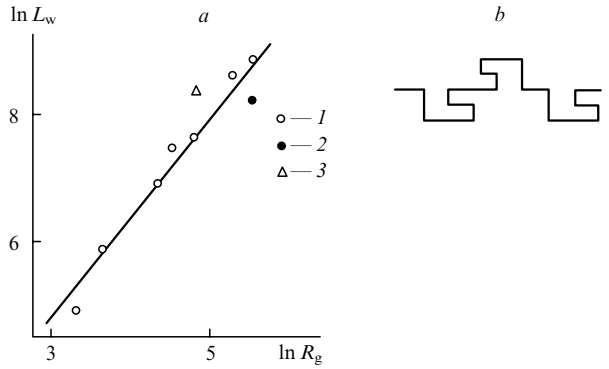


Figure 3. Chain length L_w *vs.* the radius of gyration R_g for a macromolecular coil of polystyrene (*1*), poly(methyl methacrylate) (*2*) and polyethylene (*3*) (*a*) and a variant of elements of the Koch curves having $d_f = 1.61$ (*b*).[88]

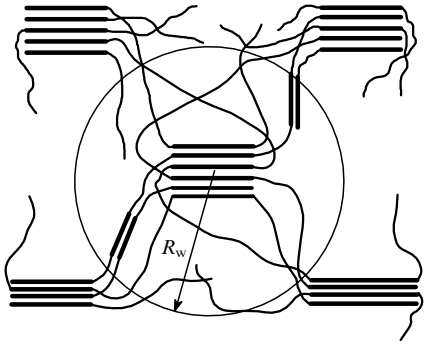


Figure 4. Cluster model of the structure of an amorphous polymer.

the Witten – Sander (WS) model.[77, 78] Such a cluster distinguished in a polymer bulk restricted by the radius R_w would possess at least two features typical of fractal clusters. One feature is self-similarity, caused by the presence of unstable clusters consisting of fewer segments than thermodynamically stable clusters (Fig. 4 shows them consisting of two segments). The other feature is that the density of particles (statistical segments) comprising the cluster would decrease on moving away from the cluster centre and thus stipulate the $\rho(L)$ dependence typical of fractals (see Fig. 1). In conformity with this dependence, it is assumed that the structure of an amorphous polymer contains sorts of 'thickened' and 'rarefied' sections. This 'thickening' of the material can be explained by assuming the existence of a local order (as opposed to the model of interpenetrating macromolecular coils, *i.e.*, the 'felt' model, proposed by Flory).[92, 93] Thus, the fractality of the structure of amorphous polymers in the $\sim 0.3 - 5.0$ nm range, shown experimentally in a number of studies,[22, 35] is confirmed indirectly by the presence of local order.

The size of a fractal cluster R_w and the number of particles in it N_r are related to each other by the following expression:[88]

$$N_r \propto R_w^{d_f}. \tag{26}$$

Let us consider the procedure for estimation of the N_r and R_w values in terms of the cluster model.[15, 86] A cluster is regarded as a multifunctional unit in a fluctuation network of macromolecular entanglements; therefore, according to Flory,[42] the reduced molecular mass M per cluster is estimated from Eqn (4). By dividing M into the molecular mass of a statistical segment, we obtain the number of particles (statistical segments) N_{st} per cluster.

The distance between the clusters R_{cl} should be taken as R_w

$$R_{cl} = 18\left(\frac{2V_{cl}}{F}\right)^{-1/3}, \tag{26a}$$

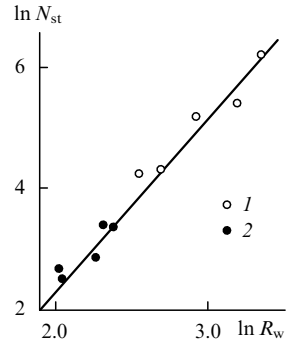


Figure 5. Number of statistical segments N_{st} in a cluster *vs.* its radius R_w for amorphous (*1*) and amorphous-crystalline (*2*) polymers under the assumption that the sizes of fractal and percolation clusters are equal.

where V_{cl} is the density of the cluster network and F is the cluster functionality.

Figure 5 presents the dependence of N_{st} on R_w for five amorphous vitreous and five amorphous-crystalline polymers.[8] It can be seen that this correlation is fully consistent with relation (26). The d_f value of the cluster structure determined from the slope of the straight line is ~ 2.75. The fractal dimension of the cluster in the WS model lies in the range of $2.25 - 2.75$,[88] which is in agreement with the above estimate.

The fractal dimension for the structure of the amorphous polymer can be found from the relation [94]

$$d_f = (d - 1)(1 + \mu), \tag{27}$$

where μ is the Poisson coefficient.

For a cluster structure with $d_f \approx 2.75$, the μ value is equal to ~ 0.375, which is consistent with the known μ values for amorphous vitreous polymers.[95, 96]

As an example of fractality displayed in polymers at a macroscopic level (a secondary structural element), we shall consider the growth of a crack in a film of amorphous vitreous polyarylatesulfone.[97] The surfaces of cracks have irregularities of at least two scales: ~ 20 μm (Fig. 6 *a*) and ~ 20 mm (Fig. 6 *b*). This provides grounds for describing them in terms of fractal models.[98 – 100] The triangular profile throughout the whole period of growth of the crack allows the use of the relationship proposed by Mosolov [98]

$$d_{sk} \propto r_{sk}^{D_{sk}/2}, \tag{28}$$

where d_{sk} is the crack opening, r_{sk} is the distance from the crack top and D_{sk} is the fractal dimension of the crack.

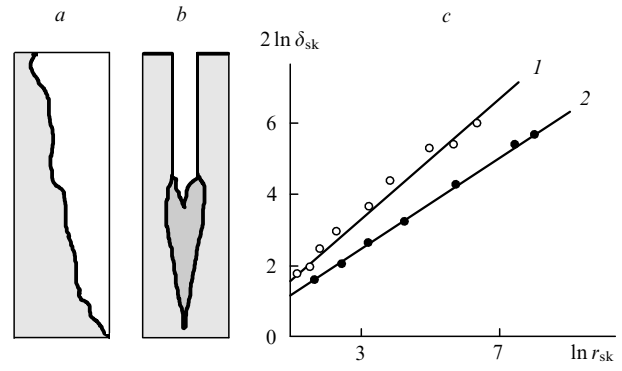


Figure 6. Crack coast-line (*a*), general view of a stable crack (*b*) and opening of the crack δ_{sk} *vs.* the distance to its top r_{sk} (*c*) for polycarbonate (*1*) and polyarylate (*2*).[8]

Figure 6 *c* shows the plots for the variation of δ_{sk} *vs.* r_{sk} for two amorphous polymers; the plots correspond to relation (28). In other words, a stable crack in polymer film samples is a stochastic fractal with the dimension $D_{sk} \approx 1.48$. The linearity of plots shown in Fig. 6 *c* reflects the self-similarity of the crack at different stages of its growth. Thus, polymers also exhibit fractal properties at the macroscopic level.

The examples considered above do not reflect the whole diversity of manifestation of fractality in polymers. Nevertheless, they help to understand the meaning of the term 'multifractality' as applied to polymers.

III. Fractal characteristics of macromolecules

Condensed systems start to behave as polymers after a certain molecular mass has been attained and a network of macromolecular entanglements or chemical nodes has been formed.[56] In consideration of condensed polymers, it is especially important to describe the sections of the macromolecule between the points of chemical cross-linking or entanglements.[55] The deformability and mobility of these sections largely determine the macroscopic properties of polymers.[56, 101] The general physical grounds which account for the fractality of these chain sections are considered below in relation to epoxy polymers.

To determine the fractality of an object, three aspects are usually considered.[12] First, as noted above, a real physical object possesses fractal properties only in a definite scale range (see Fig. 1). The boundary sizes for a macromolecular section can be determined using the data of several publications.[22, 35, 102] The lower boundary is related to the finite size of a structural element; in terms of the cluster model, this is the length of the statistical segment l_{st}

$$l_{st} = l_0 C_\infty , \tag{29}$$

where l_0 is the length of a chemical bond and C_∞ is the characteristic ratio.

For most polymers, $l_0 = 0.125$ nm (see Ref. 90), the minimum $C_\infty = 2$ (see Ref. 91); therefore, the minimum possible l_{st} is 0.25 nm. This value is in good agreement with the experimental estimate of the lower limit of fractality in polymers (~ 0.3 nm [22]) and should be accepted as the L_{min} for the chain section between chemical cross-links. The length of this section L_s can be taken as the upper limit. For most of the epoxy polymers considered, this value is in the range from ~ 1.6 to 7.4 nm, which is also consistent with the data of Refs 22 and 35.

The second aspect is associated with the self-similarity of the object considered. A section of the macromolecule between chemical cross-linking points represented by a freely jointed Kuhn chain or by a chain with free or hindered rotation about the bond [91] is simulated by a broken line having the topological dimension $d_t = 1$.[3] In the case of simulation by the freely jointed Kuhn chain, the broken line consists of N_s statistical segments of length A, each of them being simulated by a straight-line segment. These straight-line segments are standard self-similar objects but the chain sections consisting of them are self-similar only when their lengths L_s and the A values vary proportionally. For the epoxy polymers in question, this condition is fulfilled;[103] therefore, these sections are self-similar objects.[104]

Finally, the third aspect concerns determination of the fractal dimension D of an object.[12] For fractals, the condition

$$D > d_t .$$

should hold.[16] In the case where a macromolecular section between chemical cross-linking points is represented by the freely jointed Kuhn chain, the following equality should hold:[101]

$$R_s^2 = L_s A, \tag{30}$$

where R_s is the smallest (straight-line) distance between chemical cross-links.

A fractal broken line can be described by the relation [88]

$$\frac{L}{a} = \left(\frac{R}{a}\right)^D , \tag{31}$$

where L is the length of the line, R is the straight-line distance between its ends, a is the scale of measurements in the macromolecule.

By dividing both parts of Eqn (30) by A^2, we find that

$$\frac{L_s}{A} = \left(\frac{R_s}{a}\right)^2 , \tag{32}$$

i.e., a freely jointed Kuhn chain is a broken line with dimension 2 provided that condition (30) is fulfilled. Note that in this case, the chain is a fractal because $D > d_t$. Since the random-walk dimension d_w for this model of a macromolecule is also equal to 2,[66] the spectral dimension d_s of the chain can be estimated [see Eqn (8)]. For a freely jointed Kuhn chain, it is also equal to 2.

Let us consider conditions under which $d_s = 2$. For a real polymer, with allowance for the effect of excluded volume, one can write that [56]

$$D = \frac{2d_s}{\alpha - d_s} , \tag{33}$$

where

$$\alpha = d_s + \frac{2(d_s + 2)}{d + 2} . \tag{34}$$

When $D = d_s = 2$, Eqns (32) and (34) are correct only when $d = 2$. This means that the ranges of variation of the fractal dimension of a macromolecule section between cross-linking points are $d_t < D \leqslant d$ or $1 < D \leqslant 2$.

However, the freely jointed Kuhn chain is the most idealised model for a real macromolecule; therefore, there exist several corrections taking into account specific features of the polymer structure. Thus, for chains in which $L_s/A < 10$, condition (30) no longer holds. The modified condition is written as follows [91]

$$R_s^2 = L_s A - \frac{A(1 - e^{-2L_s A})}{2} . \tag{35}$$

Equation (35) points to a decrease in L_s at a constant R_s and, hence, to a decrease in D, in conformity with Eqn (31). Note that the condition $L_s/A < 10$ holds for nine of the ten specimens of epoxy polymers; this automatically means that $D < 2$.[8]

The hindrance of rotation of the macro-chain around bonds, which necessarily occurs in a vitreous polymer, accounts for the decrease in the real A value to A_{rot} according to the relation [91]

$$\sigma^2 = \frac{A}{A_{rot}} , \tag{36}$$

The hindrance parameter σ can be determined from the empirical equation [105]

$$T_g = C(\sigma - 1), \tag{37}$$

where T_g is the experimental glass transition temperature and C is a constant (for carbon-chain polymers, $C = 270$ K).

Now we can calculate non-fractal values R_s and L_s as functions of the cross-linking density ν_s using Eqn (29) and the relation [104]

$$L_s = \frac{F_{ch}}{2S\nu_s} , \tag{38}$$

where F_{ch} is the functionality of a chemical cross-linking point (hereinafter, we assume that $F_{ch} = 4$) and S is the cross-section area of the macromolecule.

The results of calculation of D as a function of ν_s for the epoxy polymers considered here using Eqn (31) with $a = A_{rot}$, $L = L_s$ and $R = R_s$ are shown in Fig. 7, curve *1*. It can be seen that the allowance for the hindered character of rotation has resulted in a monotonic decrease in D following an increase in ν_s. As has been shown,[101] this implies a decrease in the mobility (deformability) of

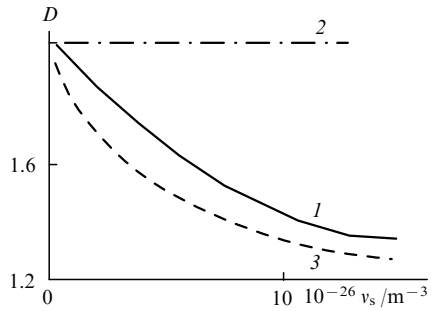


Figure 7. Fractal dimension D of a macromolecule section between chemical cross-linking points *vs.* cross-linking density ν_s for epoxy polymers based on epoxy oligomers and amino-containing curing agents. The D values were found from Eqn (31) for $a = A_{rot}$ (*1*), A (*2*) and 0.25 nm (*3*).

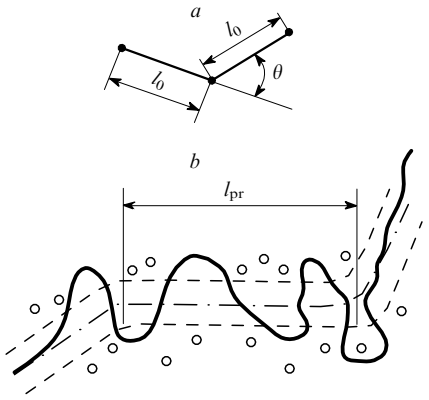


Figure 8. Schemes of two adjacent bonds of a macromolecule (*a*) and the enveloping tube (*b*).

the macromolecule section between the points of chemical cross-linking.

The calculation of D from Eqn (31) but for $a = A$ gives $D \approx 2$ irrespective of ν_s (Fig. 7, curve *2*). Finally, when persistence of the chain section is taken into account, *i.e.* the chain parameters vary according to Eqn (35), a somewhat higher D value is obtained, although the difference does not exceed $\sim 3\%$. The change in the scale of measurements also changes the fractal dimension of the chain. Curve *3* in Fig. 7 reflects the dependence of D on ν_s for $a = 0.25$ nm (*i.e.*, for the minimum size). This curve runs parallel to curve *1* but is characterised by somewhat lower D (by $\sim 3\%$–13%). Our choice of the scale of measurement of A_{rot} (or l_{st}) is due to the fact that it reflects the real state of the chain under particular conditions ('natural' scale of measurements).

Let us discuss in more detail the physical meaning of the fractal dimension D of a chain section between chemical cross-linking points (or between entanglement points). Substitution $L = L_s$, $R = R_s$ and $a = l_{st}$ in Eqn (31) gives the relation [101, 106]

$$\frac{L_s}{l_{st}} = \left(\frac{R_s}{l_{st}}\right)^D, \tag{39}$$

which implies that when $D = 1$, $L_s = R_s$, *i.e.* the chain between the cross-links is completely stretched and loses the capacity for deformation (mobility). This is consistent with the data of a publication,[51] according to which $D = 1$ corresponds to a completely uncoiled chain (see Table 2). Recall that the condition $D = 1$ means that the given section of the macromolecule has completely lost fractal properties. When $D = 2$, we obtain the maximum possible length of the chain section L_s for a fixed R_s and the greatest l_{st}, *i.e.* the chain deformability (mobility) is the most pronounced in this case. Note that the highest stretching ratio λ_{max} for a given chain section is equal to L_s/R_s. [107, 108] It is clear that $D = 2$ is attained for rubbers, and intermediate values, $1 < D < 2$, describe different degrees of mobility of a macromolecule section between chemical cross-links (entanglements). This quantitative measure of mobility is convenient because the fractional part of D provides actually a relative measure of mobility, irrespective of the structure of the macromolecule or other features of the polymers.[82]

Let us consider the physical reasons for the fractality of the macromolecule, *i.e.* for the dependence of the chain length L_s on the scale of measurement A_{rot} or l_{st}. The first reason is that L_s can change upon conformational changes in the macromolecule due to variation of C_∞, *i.e.* the bond angle θ_v can change according to the equation [91]

$$\sigma^2 = C_\infty \frac{1 - \cos\theta_v}{\cos\theta_v}. \tag{40}$$

Figure 8*a* shows schematically two consecutive bonds with the length l_0. The total length of such a section l projected onto the axis of one of the bonds is equal to

$$l = l_0 + l_0 \cos\theta_v. \tag{41}$$

It is clear that the smaller θ_v, the greater the second term in Eqn (41) and the greater L_s. The maximum L_s value is attained for tetrahedral angles ($\theta_v = 70.5^\circ$).[91] The distance between the cross-links determined in this way (we shall call it conformational length L_{conf}) is obviously equal to

$$L_{conf} = \frac{L_s l}{2l_0}. \tag{42}$$

Another physical representation of the effect in question is the use of the reptation model,[41] in which a macromolecule is assumed to be encapsulated in a 'tube' of a finite thickness (Fig. 8 *b*). In this case, the topological skeleton of the chain consists of N_{pr} units of length l_{pr}, which form a primitive path with the length

$$L_{pr} = N_{pr} l_{pr}.$$

It is also assumed that the ends of fragments of the primitive path with the length l_{pr} are fixed in a definite manner; therefore, the N_{pr} and L_{pr} values can be found fairly easily using l_{pr}. The L_{pr} value can be expressed as follows:[41]

$$L_{pr} = L_s \frac{A_{rot}}{l_{pr}}, \tag{43}$$

where l_{pr} is assumed to be equal to the distance between clusters R_{cl}, which can be calculated from Eqn (26a).

The length of the fractal broken line L_f is expressed in the following way:[3]

$$L_f = L' a^{1-D}, \tag{44}$$

where $L' > 1$ is the length of the non-fractal line.

Since the L_s value determined using Eqn (38) is calculated, in the first approximation, as the length of a cylinder with the cross-section area S, *i.e.* of a non-fractal object, it can be assumed that $L' \approx L_s$. If the two above examples point to the presence of fractal properties of a section between chemical cross-links (entanglements), the following relation should be obeyed:

$$L_f \approx L_{conf} \approx L_{pr}. \tag{45}$$

Relation (45) actually holds (with a deviation of $\pm 20\%$) for epoxy polymers based on bisphenol A and cured by diamine (EP-1) or anhydride (EP-2) (Fig. 9).[47] This indicates that the fractality of the macromolecule section between chemical cross-linking points (entanglements) in a vitreous polymer is due to known mechanisms of the change in the statistical rigidity.

It follows from Eqn (39) that the loss of fractality by a chain section, irrespective of the scale of measurements, takes place in the case of full stretching of this section between cross-linking

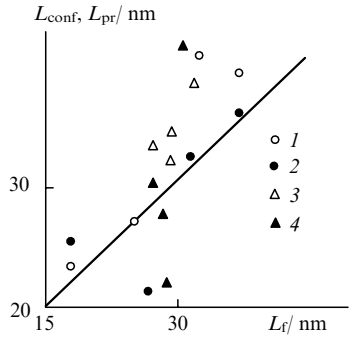


Figure 9. Relationships between the conformational length L_{conf} (*1*, *3*) and primitive path L_{pr} (*2*, *4*) of the chain section between chemical cross-linking points and its fractal length L_f for EP-1 (*1*, *2*) and EP-2 (*3*, *4*).

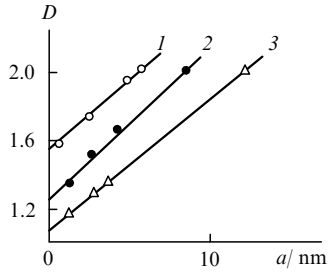


Figure 10. Fractal dimension of the macromolecule section between chemical cross-linking point (*D*) *vs.* scale of measurement *a* for EP-1. $v_s \times 10^{-27}$/ m^{-3}: (*1*) 0.2, (*2*) 0.6, (*3*) 1.7.

points (entanglements), *i.e.* when $L_s = R_s$. In addition, for $a \to 0$, the $L(a)$ value would tend to a final limit equal to the length of the straight line. Figure 10 shows the $D(a)$ plots for EP-1. It can be seen that, when $a \to 0$, the fractality of the chain section between cross-linking points is retained. Therefore, the behaviour of this section of a macromolecule is more intricate than that of a mere fractal broken line; this can be due to a more complex structure of the macromolecule. Indeed, transition to a non-fractal behaviour requires not only that condition $L_s = R_s$ be fulfilled, as for an ordinary broken line, for example, for a coast-line, but also that a conformation condition — Eqn (30) — be fulfilled. In this case, it is necessary that the bond angle θ_v reach a value which complies with the equality (for $l_{st} = A$)

$$C_\infty = \frac{A}{l_0}\cos\frac{\theta_v}{2}. \tag{46}$$

A chain for which $D \neq 1$ can be referred to as 'true fractal'.

Examination of Eqns (26a) and (38) leads to yet another, at least formal, reason for the fractal properties of the section of a macromolecule between the cross-links. For a given cross-linking density, the L_s value (unlike R_s) depends on the cross-sectional area S of the macromolecule, which should also result in the variation of D. Figure 11 shows the dependences of D on S for two arbitrary v_s values, namely, 1×10^{27} and 2×10^{27} m^{-3}. It can be seen that D rapidly decreases as S increases; when $S \approx 0.80$ and 0.55 nm^2, respectively, D reaches the lower limit ($D = 1$). This implies full 'freezing' of the molecular mobility of the chain,[101] which should result in a high fragility of the polymer. This assumption is confirmed in practice. It is known that polystyrene and poly(methyl methacrylate) are fragile polymers ($S = 0.698$ and 0.638 nm^2, respectively) and poly(n-dodecyl methacrylate) and poly(n-octyl methacrylate) are highly fragile polymers ($S = 1.766$ and 1.351 nm^2, respectively).[109]

Thus, the section of the macromolecule between chemical cross-links and physical entanglements possesses fractal properties. This is due to the fact that the length of this section is shorter than the size of the macromolecule. This factor is due to various

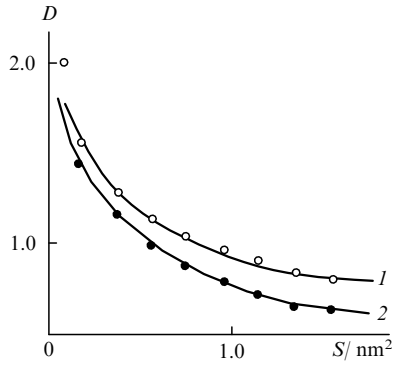


Figure 11. Fractal dimension of a section of macromolecule between chemical cross-linking points (*D*) *vs.* cross-sectional area of the macromolecule *S*.
$v_s \times 10^{-27}$/ m^{-3}: (*1*) 1, (*2*) 2.

steric restrictions, which induce deviations from the behavior predicted by Eqn (30). In the general case, Eqn (30) is valid for a non-perturbed (quasi-equilibrium) coil;[32] therefore, the fractality of the chain section considered can be interpreted as being due to the deviation from the quasi-equilibrium state.[12] The deviation changes the degree of the 'sinuosity' of the macromolecular section (*i.e.* the length of the statistical segment); therefore, the l_{st} (or A, or A_{rot}) value can be considered to be a 'natural' scale of measurement. Since the structure of a macromolecule is more complex than the geometric image represented by a broken line, its behaviour would also be more complicated; this is confirmed by the change in D when $a \to 0$. In other words, the section of a macromolecule between cross-links has configurational fractal properties, stipulated by the mutual arrangement of the rigidity sections of the macromolecule, and conformational fractal properties, caused by the state of the bonds within this rigidity section (statistical segment).

1. The dimension of the sections of a macromolecule between topological fixing points

A cross-linked polymer is formally one giant macromolecule (fractal cluster); therefore, the models considered above provide the dimension d_f of exactly this cluster. The Vilgis concept [60, 61] assumes the existence of several clusters of this type and linear macromolecules between them. In practice, parameters used more widely are the density of the network of nodes (chemical cross-links) v_s or the molecular mass of the macromolecular section between the cross-links M_s, which are related to each other in the following way:

$$v_s = \frac{\rho N_A}{M_s}, \tag{46a}$$

where N_A is the Avogadro number and ρ is the polymer density.

In a study by Sandakov *et al.*,[49] the term 'molecule' for cross-linked polymers was used to denote only a section of the macromolecule with the molecular mass M_s, because it is known [43] that it is the parameters v_s and M_s that determine the properties of network polymers. In addition, the difference between the scales of fractality of a big macromolecular cluster and the polymer structure in the vitreous state should be taken into account, *i.e.* one should have in view lengths of the order of $\sim 0.3-5.0$ nm where a macromolecule is a fractal.[22]

Below we consider practical aspects of the estimation of the fractal dimension D of a macromolecule section between chemical cross-linking points with allowance for these statements as well as for those considered in the preceding Sections. This approach differs fundamentally from that of the Cates [55] and Vilgis models.[60, 61] All the foregoing is valid not only for a network of chemical bonds but also for a network of macromolecular entanglements in linear polymers.

Several methods for the estimation of the D value exist. One method makes use of the relation [110]

$$D = \frac{\ln n_{st}}{\ln l_{st}}, \quad (47)$$

where n_{st} is the number of statistical segments of length l_{st} in a chain fragment between entanglements (chemical cross-links).

Yet another variant of calculation of D is given by Eqn (39). The following relation has been obtained:[111]

$$\frac{2}{\varphi_{cl}} = C_{\infty}^{D}, \quad (48)$$

where φ_{cl} is the relative part of local order (clusters) in the polymer.

The relationship between D and d_f [see Eqn (27)] is reflected by the expression:[112, 113]

$$D = \frac{\ln n_{st}}{\ln(4 - d_f) - \ln(3 - d_f)}. \quad (49)$$

The D values estimated using Eqns (39) and (47)–(49) vary from 1 to 2.

The use of fractal analysis makes it possible to relate molecular parameters to characteristics of supermolecular structure of polymers. Figure 12 illustrates the linear correlation between D and d_f [d_f was estimated from Eqn (27)] for epoxy polymers. When the molecular mobility is suppressed ($D = 1$), the structure of the polymer has the fractal dimension $d_f = 2.5$, which corresponds to $\mu = 0.25$. The given value of the Poisson coefficient corresponds to the boundary of ideally brittle structure; at $\mu < 0.25$, the polymer is collapsed without viscoelastic or plastic dissipation of energy.[3] This is fully consistent with the Kausch conclusion[114] stating that any increase in the molecular mobility enhances dissipation of the mechanical energy supplied from the outside and, as a consequence, increases plasticity of the polymer. When $D = 2$ the d_f value is equal to 3, which corresponds to $\mu = 0.5$, typical of the rubbery state.

Figure 12*b* shows the variation of D *vs.* v_s for the epoxy polymers considered here. The dependence is non-linear, the D value decreases with an increase in v_s; even for small v_s values, a substantial decay in D is observed. It is of interest that the end of this decay and transition to a much slower decrease in D takes place at $v_s \approx 8 \times 10^{26}$ m^{-3}, which corresponds to ~ 10 monomer units between the cross-links. Actually, this can be interpreted as transition to densely cross-linked epoxy polymers in which an increase in v_s influences the suppression of the molecular mobility to a substantially lower degree than in the region where $v_s = 0.8 \times 10^{27}$ m^{-3} (see Ref. 8).

If the conformational and/or physical state of the section between cross-links are assumed to coincide with that of the whole macromolecule (see Table 2), the plot shown in Fig. 12*b* allows one to judge the nature and the ranges of variation of these states. The first characteristic dimension $D = 2$ corresponds to the state of a statistical coil in an ideal solvent, the second one $D \approx 1.67$ corresponds to an impermeable coil in a good solvent, the third one $D = 1.50$ is matched by a permeable coil (the state typical of rigid-chain polymers), and the fourth value, $D = 1$, describes a completely uncoiled macromolecule.[50] It can be assumed that the increase in the cross-linking density between the above D values is accompanied by gradual transition from a state with greater D to a state with smaller D. Thus, depending on v_s, a network polymer can be both a rubber and a rigid-chain polymer.[115] Therefore, it is evident that the knowledge of these regularities is important for controlling the properties of network polymers.

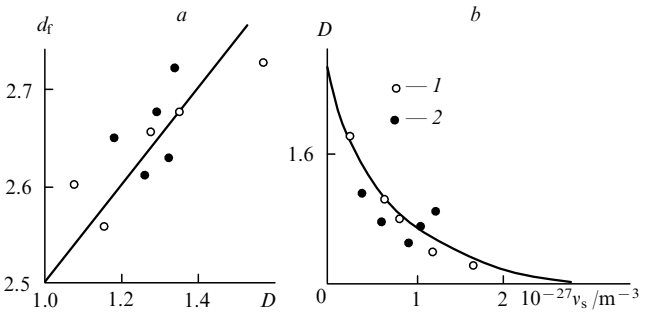


Figure 12. Correlation between fractal dimensions of the structure d_f and the chain section between chemical cross-linking points D (*a*) and the $D(v_s)$ dependence (*b*) for EP-1 (*1*) and EP-2 (*2*).[106]
The straight line was drawn through the points: $D = 1.0$, $d_f = 2.5$ and $D = 2.0$, $d_f = 3.0$.

Now we attempt to estimate D within the framework of the theoretical views on polymer fractals.[22, 35, 55, 60–63] It is assumed [66] that the fractal dimensions d_s, d_w and D are related to one another *via* an expression similar to Eqn (8). The relationship between the parameters d_s and D has been considered.[65] It is believed that d_s is a dynamic value which responds to a change in the conditions of the interaction of a macromolecule with its surrounding and D is a static parameter. However, in our opinion, the opposite situation occurs in reality; this is indicated by the following facts, some of which have been noted above. It has been shown experimentally [69] that a twofold increase in the cross-linking density does not change d_s, while, according to the plot shown in Fig. 12*b*, v_s has an appreciable influence on D. Moreover, the monomer and the cross-linked epoxy polymer have nearly identical d_s values (see Table 4). Helman *et al.*[66] proposed a fractal model in which they employ the notion of weightless bridges. In accordance with this model, d_s is equal to D when the concentration of these bridges is relatively high. However, theoretical analysis and computer simulation [10, 67] show that the inclusion into consideration of bridges of a finite length does not change the spectral dimension of the system. With allowance for this fact, it was assumed that the d_s value would be equal to that determined experimentally for an epoxy polymer in a three-dimensional space, $d_s = 1.44$ (see Ref. 69).

Two hypotheses can be used to estimate d_w — the Alexander–Orbach (AO) and Aharoni–Stauffer (AS) hypotheses.[10] The AO hypothesis is based on the following relation:

$$d_w = \frac{3}{2} d_f,$$

while the AS hypothesis assumes the relation

$$d_w = 1 + d_f.$$

It is considered that d_w is determined by the properties of the supermolecular structure of epoxy polymers, namely, by the degree of local order in them. This assumption arises due to the well-known succession of relationships between the diffusion process and d_w, [28] between the diffusion process and the fluctuation free volume f_{fv}, [116] and between f_{fv} and the cluster structure.[117] Therefore, the fractal dimension of the cluster structure of cross-linked polymers,[102, 107] estimated from Eqn (27), is taken to be d_f. Since the D value is determined for an Euclidean space with $d = 2$, it was also assumed in Eqn (27) that $d = 2$. The d_s value was found for a three-dimensional space; therefore, a graph [118] for converting d_s from three- to two-dimensional space was used in subsequent calculations. The D values were further calculated from Eqn (8) in terms of the AO and AS hypotheses. Figure 13 shows the dependences of D on v_s calculated from Eqns (8) and (39). The dependences of D on v_s and the absolute magnitudes of D are in good agreement, especially when the AO hypothesis is used. When v_s is low, the D values calculated from Eqn (39) deviate towards the curve estimated using the AO hypothesis. Nevertheless, the discrepancy between the calculations by two methods does not exceed 10%.

Thus, the fractal dimension of a section of the macromolecule between chemical cross-linking points in network polymers varies

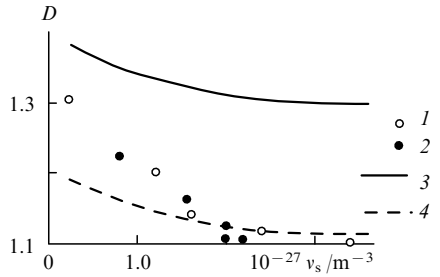


Figure 13. Fractal dimension of the chain section between chemical cross-linking points D *vs*. cross-linking density v_s.
Calculation using Eqn (39) for EP-1 (*1*) and EP-2 (*2*); calculation using Eqn (8) for EP-1 and EP-2 in terms of the AS (*3*) and AO (*4*) hypotheses.

over limits close to those predicted for a fractal broken line, *i.e.* $1 \leqslant D \leqslant 2$. The dimension D can serve as a measure of the molecular mobility and is related to the fractal dimension of the cluster structure of epoxy polymers d_f. The dependence of D on d_f can also be derived theoretically. The calculation procedures proposed take into account the influence on D of characteristics of the molecular and topological structural levels of cross-linked polymers.

2. The concept of macromolecular skeletons

a. The model of a network polymer

The model of network polymers considered below describes quantitatively the formation of structure (and, hence, properties) and is based on fundamental principles of physics. The initial parameters used for cross-linked systems are the v_s value (topological characteristics) and some generally accepted molecular parameters. Since the chemical cross-linking processes are complex, the model makes use of the simplest scheme of structure formation, which does not take into account, for example, the decrease in the rate of structure formation with time when one structure element starts to influence the conditions of formation of an adjacent element. An example of taking account of effects of this type has been reported.[118] Although this scheme is simple, it provides a quantitative description of the processes considered and the structures formed.

One point of the model under discussion is estimation of the relationship between v_s and the level of local order in the structure of epoxy polymers, which is characterised by the density V_{cl} of the cluster network of macromolecular entanglements.[101–103] A parameter characterising the level of local order more rigorously is the fraction of clusters φ_{cl} in the polymer.

Curing is supposed to be a turbulent process because it requires mobility of structural elements and takes place in a viscous medium. In addition, transition to a turbulent mode implies an increase in the degree of ordering, *i.e.* self-organisation of dissipative structures such as clusters.[119] A fundamental property of turbulent flows is fractality of turbulent structures.[3, 10] It is generally believed that dissipation of energy in three-dimensional turbulent flows is concentrated on a set with a non-integral fractal dimension. However, experimental data on the beginning of fluctuations indicate that the small-scale properties of a turbulent flow cannot be described by virtue of fractals.[3] Therefore, turbulent dissipative structures are described using 'non-homogeneous fractals,' the rules of formation of which are chosen at random at each step of scale hierarchy in accordance with some probability distribution.[120, 121] In this case, the transfer of energy is described by virtue of random fragmentation model with the assumption that no correlations exist between stages of the process. Nevertheless, it is possible to calculate the fractal dimension of turbulent structures (D_f), which is defined by the relation

$$\langle N_n \rangle \sim L_n^{-D_f}, \tag{50}$$

where N_n is the number of active vortices at an n-th fragmentation step, L_n is the scale of the n-th vortex, and D is estimated using the following equation:[10]

$$D_f = 3 + \log_2 \beta, \tag{51}$$

in which β is the fraction of the volume occupied by vortices of the scale L_n.

As a first approximation, it can be assumed that $D_f = d_f^t$, where d_f^t is the fractal dimension of the topological structure of the polymer, which can be found from Eqn (27).

It is clear that the chain fragments with the molecular mass M_s are considered in a plane ($d = 2$) and the formation of clusters is discussed in a volume ($d = 3$). The D value calculated from Eqn (39) for a two-dimensional fractal can be used to find the value for a three-dimensional fractal by applying Eqn (27) to the dimension d_f^t. This method is not highly accurate but simple. Equation (51) makes it possible to determine the fraction of volume β occupied by vortices of the L_n scale. Assuming that the β and φ_{cl} values are equal, the V_{cl} value can be calculated from the relation

$$V_{cl} = \frac{\varphi_{cl}}{S l_0 C_\infty}.$$

Comparison of the V_{cl} values found in this way with those obtained experimentally [47] for systems EP-1 and EP-2 showed that the two methods provide the same order of magnitude. Nevertheless, to attain better agreement between the results, it can be assumed that not all the active turbulent vortices are converted into local order regions; in general, this is obvious due to the fluctuational nature of these regions.[89] This means that $\varphi_{cl} = C\beta$, where C is a proportionality coefficient. Assuming that for EP-1 and EP-2, $C = 0.6$, we obtain a much better quantitative agreement between experimental and calculated data. It is clear that the coefficient C reflects the influence of variable characteristics of curing such as temperature, time, viscosity of the medium, *etc*. The fact that the dimension of non-homogeneous fractal D_f is always greater than the dimension of the corresponding homogeneous fractal d_f^t might serve as yet another reason for the inconsistency between the φ_{cl} and β values, mentioned above.[122] The condition $D_f > d_f^t$ implies a decrease in β in the calculations using Eqn (51).

Fractality of the structures of polymers influences their properties. According to modern concepts,[123–125] the glass transition of amorphous polymers is regarded as the formation of 'frozen' local order (dissipative structures). Generally, for amorphous systems, this is considered to be a complex and hierarchically multistage process. The first stage involves the formation of seeds of microcrystals, which are unable to grow and serve as a sort of substrate for deposition of amorphous clusters. The second stage is characterised by self-organisation of mesoclusters.[126] As applied to the glass transition of polymers, these processes can be specified in the following way. The first stage starts at the temperature of so-called liquid–liquid transition T_{ll}, in which regions of dynamic short-lived local order are formed.[23] At the glass transition temperature, avalanche-like accumulation of clusters takes place, which characterises the formation of 'frozen' local order (the second stage). For this process,

$$\tau^* \propto (R^*)^{d_f}, \tag{51a}$$

where τ^* is the time before the onset of this process and R^* is the critical cluster size.[98]

Since the temperature–time superposition is correct for polymers, we assume that $R^* \propto l_{st}$ and write relation (51a) in the following form

$$T_g \propto l_{st}^{-\alpha}.$$

The dependence of the experimental T_g values [112] on l_{st} for epoxy polymers can be represented by a correlation function. In addition, $\alpha \simeq 0.28$, which complies with the necessary condition

$\alpha = d - d_f$.[88] Hence, the change in T_g upon the variation of v_s is also an indication of the fractal structure of network polymers.

Note that the behaviour of network polymers is in agreement with several other fundamental physical principles. Let us illustrate this by two examples. An integral stoichiometry implies stability and ordering of the structure of a compound.[3] This is confirmed by the data of Beloshenko *et al.*,[102] according to which the maximum degree of local ordering in epoxy polymers is attained when an oligomer and a curing agent are taken in stoichiometric amounts, *i.e.* when $K = 1.0$ (or is close to 1).

Structure parameters and characteristics of properties of epoxy polymers are not random values either. Thus the length of statistical segment l_{st} obeys the automodelling relation

$$\frac{l_{st\,i}}{l_{st(i+1)}} = \Delta^{1/m}, \tag{52}$$

where $\Delta = 10$ and m varies according to a geometric progression law

$$m = 2, 4, 8, 16, 32, ..., 2^n, ..., \infty. \tag{53}$$

Hence, formation of the structure and properties of epoxy polymers during curing is determined by fundamental physical principles. This is accompanied by the change in the characteristic ratio C_∞ (molecular characteristics), although the structure of the macromolecule remains invariant. The use of the above physical principles even in the simplest version provides a correct description of the structure and properties of network polymers.

b. Scaling representation of a macromolecule

A number of methods exist for the modelling of polymers at a molecular level. One of the most widely used methods is scaling presentation,[52] according to which the diameter ø of the 'tube' in which the macromolecule is enclosed (it is equal to the distance between the entanglement points) can be estimated from the ratio [72]

$$ø^2 = C_\infty \frac{M_s l_0^2}{m_0}. \tag{54}$$

The main difference between physical entanglements (loops) and chemical cross-links is that the former allow creeping of chains. The density of both types of link are determined using the same rubber elasticity equation, a factor of 0.8 being frequently added to take creeping into account.[72]

Yet another representation of a macromolecular chain as a fractal is considered below. Olemskoy and Flat [127] have noted that the concept of fractals rather than description of an observed geometric image is usually applied to condensed media. As regards a macromolecule, modelled by a freely jointed chain consisting of statistical segments, one can hardly find a geometrical image more vivid than a fractal broken line. In addition, it should be noted that representation of a macromolecule by either one-dimensional (as a curve) or three-dimensional (as a cylinder) object appears to be a fairly rough approximation in view of the real structure of a macromolecule, *i.e.* the presence of side chains, flexible bonds, rigid segments, *etc.*

As noted above, a change in the density of chemical cross-linking v_s in epoxy polymers results in an extremal variation of the characteristic ratio C_∞ with the minimum $K \simeq 1.0$.[115] If the section of a macromolecule between chemical cross-links is modelled by a freely jointed chain, the use of known L_s and l_{st} values results in a typical fractal dependence [119]

$$N_{st}(\xi l_{st}) = \xi^{-D} N_{st}(l_{st}),\ \xi < 1, \tag{55}$$

where N_{st} is the number of statistical segments per fragment of a macromolecule with the molecular mass M_s, and ξ is a similarity parameter.

With the assumption that $L_s = \text{const}$ and $K = 1.0$, $\xi = 0.85$ was obtained; with $L_s = \text{const}$ and $K > 1.0$, the calculations gave $\xi = (0.85)^{1/2} = 0.926$. The calculation of the dimension D from Eqn (55) gave 1.17. Thus, when the condition mentioned above is fulfilled, the section of a macromolecule between chemical cross-linking points can be represented as a fractal. Variation of K changes the cross-linking density v_s and, hence, L_s. As a consequence, the chain ceases to be a self-similar fractal. Nevertheless, it still can be modelled by a non-homogeneous fractal with the same fragmentation step but with a variable D value, determined from relation (39). The D values calculated in this way are listed in Table 6.

Table 6. Calculated molecular characteristics of epoxy polymers.[8]

Polymer	K	D	C_∞		
			I	II	III
EP-1	0.50	2.06	5.23	4.83	5.28
	0.75	1.60	4.32	6.97	3.50
	1.00	1.25	3.38	9.94	3.68
	1.25	1.35	3.75	8.89	3.19
	1.50	1.50	4.05	7.68	3.34
EP-2	0.50	1.85	5.27	6.54	5.35
	0.75	1.43	3.98	8.89	4.69
	1.00	1.32	3.40	9.24	3.37
	1.25	1.35	3.70	9.24	3.90
	1.50	1.55	4.10	7.96	4.29

Note. The following designations are used: I — data of Ref. 121, II — calculation by Eqn (54), III — calculation by Eqn (57).

The results of calculation of the characteristic ratio C_∞ from Eqn (54) are inconsistent in kind with the data obtained by Jean *et al.*[128] Indeed, the maximum rather than the minimum C_∞ is attained at $K = 1.0$. Since

$$ø^2 \propto v_s^{-2/3},\ M_s \propto v_s^{-1},$$

then, according to Eqn (54), the C_∞ value should be proportional to $v_s^{1/2}$. In other words, an increase in the density of cross-links should increase the chain flexibility, which is inconsistent with the extremal increase in the glass transition temperature of epoxy polymers.[115, 129]

Let us consider the reasons for this inconsistency.

Since

$$C_\infty l_0 = l_{st},\ \frac{M l_0}{m} = L_0,$$

multiplication and division of Eqn (54) by l_{st}^2 gives the relation [8]

$$\frac{L_0}{l_{st}} = \left(\frac{R_s}{l_{st}}\right)^2, \tag{56}$$

which is similar to Eqn (39). Comparison of Eqns (39) and (56) shows that the scaling relation (54) is a specific case of the fractal formula (39) for $D = 2$. For the epoxy polymers considered, condition $D = 2$ does not hold (see Table 6); this may account for the discrepancy found. Using relations (39) and (56), the scaling equation (54) can be written in a more general form

$$a^D = C_\infty^{D-1} \frac{M_s l_0^D}{m}. \tag{57}$$

The calculation of C_∞ using Eqn (57) give values that are in good agreement with the results obtained by Jean *et al.*[128]

It has been shown [90] that in the case of linear polymers, the following empirical correlation is obeyed for physical entanglements

$$R_s \simeq 10\, C_\infty. \tag{58}$$

Taking into account the data presented above, the same (or similar) correlation should be expected for chemical cross-links in network polymers.

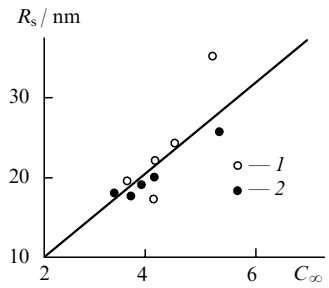


Figure 14. Distance between chemical cross-linking points R_s *vs.* characteristic ratio C_∞ for EP-1 (*1*) and EP-2 (*2*).[8]

The relationship between the C_∞ values found using Eqn (57) and R_s calculated using Eqn (26a) is linear

$$R_s \simeq 5C_\infty, \tag{59}$$

which is illustrated by Fig. 14.

Equations (58) and (59) are qualitatively similar and the discrepancy of numerical coefficients can be due to the approximate character of these relations and to the difference between the methods used to calculate R_s.[130]

Recall that the parameter D characterises the degree of deformability (mobility) of a macromolecule fragment between chemical cross-linking points. Indeed, an increase in the chain flexibility brings about an increase in C_∞, *i.e.* an increase in D. It should be noted that extrapolation of straight line $D(C_\infty)$ to $D = 1$ gives $C_\infty \simeq 2.55$; evidently, this is the limiting value for epoxy polymers considered. It is also noteworthy that it is close to C_∞ for a linear polymer with a similar structure, for example, for polycarbonate, which has $C_\infty = 2.4$.[90]

Apparently, the deformability of a macromolecule in vitreous epoxy polymers is determined not only by their molecular characteristics but also by supermolecular (supersegmental) 'frozen' structure, which can be characterised quantitatively in terms of the cluster model. It should be borne in mind that an amorphous polymer contains regions of local order (clusters) and that fixing of one or several statistical chain segments in a cluster should change the D value. The most probable reason for the change in D is that the fixed segment becomes expelled from the freely jointed chain, as it has lost its mobility in the junction points. Evidently, this decreases the L_s value in Eqn (39) by l_{st} and, finally, induces a decrease in D. Thus in the case of epoxy polymer EP-1, elimination of one statistical segment induces a decrease in D from 2.06 to 1.73; when two segments are eliminated, D decreases to 1.65; in the case of three segments, it decreases to 1.56, *etc*. In the absence of 'frozen' local order, *i.e.*, for rubbers ($\varphi_{cl} = 0$), $D = 2$ and the loss of chain mobility (deformability) is attained at $\varphi_{cl} \simeq 0.65$. The opposite effect is also possible; an increase in v_s induces a decrease in D, *i.e.* the chain becomes more taut, which should increase the level of local order.[131]

In the case of linear polymers, the network of macromolecular entanglements is the analogue of the network of chemical bonds; their density V_{en} is determined at $T > T_g$.

Thus, relation (54) is a specific case of a more general fractal relation (57) and is applicable only to rubbers, for which it has actually been derived.

c. Estimation of structural parameters

The cited examples demonstrate the capacity and the prospects of using fractal concepts for the description of macromolecular characteristics of network and linear polymers. The change in the C_∞ value induced by variation of v_s or V_{en} implies that an absolutely different polymer can be formed although the chemical composition of the macromolecule has remained almost the same. This 'new' polymer would have different molecular characteristics (C_∞, D), a different supersegmental structure (V_{cl}, φ_{cl}), and other properties (glass transition temperature T_g, elasticity modulus E, *etc*.). Equation (54) gives the maximum C_∞ value possible for the given v_s (see Table 6); the minimum values can be obtained by extrapolating the straight line $D(C_\infty)$ to $D = 1$.

At present, vitreous network polymers are mainly characterised by the v_s value.[43] However, one network polymer with constant v_s can possess different properties, for example, different glass transition temperatures.[132] This is explained by the change in the supermolecular structure of a network polymer during physical ageing, namely, by an increase in the level of local order. This effect has been described quantitatively in terms of the cluster model. In turn, the level of local order determines the fractal dimension d_f of the supermolecular (supersegmental) structure of the polymer.[8] Thus, it becomes possible to predict structural characteristics (and, hence, properties) of network polymers in the vitreous state based on the degree of chemical cross-linking up to the gelation point.

Analysis of the relationship between v_s and d_f for the epoxy polymers considered showed that an increase in the fractal dimension of the framework to the gelation point induces a decrease in the fractal dimension of the supermolecular (supersegmental) structure of the network polymer in the glassy state.

It has been noted in the Introduction that description of fractal structures requires, at least, two dimensions, d_s and d_f, at a constant d value.[27] However, the fractal concept is a mathematical model, which does not provide identification of the specific features of the polymer structure. Therefore, in order to use the parameters d_s and d_f in practice (for instance, in computer simulation), one has to find out which elements of the polymer structure (in particular, of network polymers) they embody. It is known[55] that d_s characterises the degree of connectivity of the framework and d_f (which might be time-dependent) refers to the structure of this framework. The d_f value can be found from Eqn (27), which indicates that d_f is a function only of the Poisson coefficient μ (for fixed d). For amorphous polymers, μ is determined by the degree of local order;[46] hence, this structural factor also determines d_f. As regards the spectral dimension d_s, it appears to be related in one way or another to the framework formed by chemical cross-links. This suggestion was based on the results of two studies by Kozlov *et al.*[115,133] In the former study, the relationships between v_s and the degree of local order and between d_s and d_f were elucidated. The latter study demonstrated the variation of properties of epoxy polymers with time (during physical ageing) following the change in the level of local order (or d_f) with v_s remaining invariant.

The d_s value can be calculated from Eqn (8). For estimating the dimension d_w, needed for this purpose, several relations exist;[23,36,55,60,122,134,135] they give somewhat different (to within ~20%) absolute magnitudes of this parameter. If the variant of constant d_w is chosen and the model of 'lattice animals' ($d = 3$) is used for describing branched polymers, the dependence of d_s on v_s would follow a somewhat unexpected pattern. According to this dependence, an increase in the density of cross-linking points results in lower d_s and, hence, in lower connectivity of the macromolecular framework of chemical cross-links. It is noteworthy that for great v_s, the d_s value approaches asymptotically the experimental spectral dimensions of epoxy polymers.[22,35,69] This finding can be interpreted in terms of the generally accepted models of the structure (or, more precisely, morphology) of network polymers.[136]

The main morphological unit of densely cross-linked epoxy polymers is a globule. It is a local thickening of a molecular space network the packing density in which is higher than the average density. During etching of fractured surfaces of epoxy polymers, this thickening is revealed as a discrete particle — a globule. The non-homogeneity of network polymers is due to both the kinetics of formation of a three-dimensional network and the presence of associates in the initial oligomers.[136]

Two variants of construction of a supermolecular (globular) structure are possible: (a) accrete globules with a hexagonal or cubic packing form a strong continuous skeleton in which the role

of inter-globule defective areas is insignificant; (b) densely cross-linked globules (grains) are located in a sparse-network matrix and do not contact directly one another.

The former variant of morphology seems to be more frequently encountered. An increase in the concentration of a cross-linking agent induces simultaneous generation of a large number of chemical reaction centres; this is confirmed indirectly by a decrease in the size and the increase in the number of globules.[116] This results in a smaller size and a greater number of inter-globule defective areas; thus, the connectivity of the skeleton diminishes (defective areas act as sorts of skeletal discontinuities) and, hence, d_s decreases.

In the case where the morphology of a network polymer corresponds to the second variant, its structure can be represented as a mixture of arbitrary polymer fractals in the vicinity of the gelation point; the spectral dimension of the globule is d_s and that of the inter-globule area is δ_s. The δ_s value can be estimated using the relation [60]

$$d_f = d_s \frac{(d+1)(2-\delta_s)}{(2+d_s-2\delta_s)}.$$

As a first approximation, it was assumed in this relation that the spectral dimensions of the structures of the epoxy polymer and the globules are equal. It was found that the dependence of δ_s on v_s for epoxy polymers shows parallel variation of d_s and δ_s upon the variation of v_s provided that $d_s > \delta_s$.[60] This condition indicates that the skeleton in the inter-globular gaps is less connected than the globules themselves because it is more defective.

Thus, the density of chemical cross-linking points cannot serve as an index for the connectivity of the macromolecular skeleton of network polymers. This makes impossible the use of v_s to characterise the structure of network polymers in a computer simulation, which follows from the results presented above. The d_s value, which provides determination of elastic properties, may serve as a suitable parameter. However, to estimate other properties, one more parameter is required, which would characterise the degree of thermodynamic nonequilibrium of the structures of vitreous polymers. This role can be played by d_f or the density of the cluster network of physical entanglements V_{cl},[47] or by the proportion of clusters φ_{cl}.[137] For instance, the necessity to take into account d_s, V_{cl} or φ_{cl} for calculating the yield point from known elasticity modulus has been demonstrated by Beloshenko and Kozlov.[47] Therefore, the frequently encountered correlations between properties of network polymers and v_s can serve only as an illustration. The use of two parameters (for example, d_s and d_f with a constant d) is a mandatory (fundamental) condition which follows from the fractality of intermolecular frameworks of vitreous polymers; in turn, the fractality is a consequence of thermodynamic nonequilibrium of this structure.

3. Description of molecular mobility using fractal characteristics

The problems of molecular mobility in polymers have always received considerable attention.[32, 95, 138] The reasons are obvious — polymers are thermodynamically nonequlibrium solids, their physical properties being determined by molecular relaxation processes occurring in them; these processes, in turn, depend on specific structural features of molecular chains and the structural organisation of polymers.[138] However, there is no consensus regarding the parameters describing these processes. In particular, it is assumed that fast relaxations are determined by the mobility of free chains located between densely packed regions, which are simultaneously the nodes of the network of physical entanglements in a macromolecule. This interpretation fully complies with the main statements of the cluster model for the structure of amorphous polymers,[15] which provides quantitative description of structural elements. The relationship between the cluster model and fractal analysis can be formulated as follows: fractal analysis gives general physical parameters, while the cluster model makes them more specific using particular characteristics of polymers.

Yet another important aspect is worth noting. The above interpretation of the structure of amorphous polymers refers to elastomers. Extension of these notions to vitreous amorphous polymers implies 'freezing' of densely packed regions, *i.e.* a sharp increase in their lifetimes. The fractal forms of macromolecules, macromolecular coils formed during nonequilibrium physico-chemical processes are retained (remain 'frozen') in polymers. This suggests that the main factor determining the molecular mobility in the vitreous state is the mobility of chain fragments between the points of fixing.[111]

The fractal dimension D has been chosen as the structural factor characterising the level of molecular mobility;[111] this was done for the following reasons. First, a chain fragment between the points of fixing is a self-similar object having a dimension differing from the topological dimension, *i.e.* it is a fractal by definition.[107] Second, it was shown[101] that D with the range of variation $1 < D \leqslant 2$ characterises exactly the molecular mobility of a chain fragment in loosely packed regions.[138] The condition $D = 1$ implies stretching of this chain fragment and loss of fractal properties and mobility. In terms of relaxation spectroscopy, this means that $\tan\delta = 0$, where $\tan\delta$ is the mechanical (or dielectric) loss tangent. The condition $D = 2$ means the maximum possible mobility of the chain section, which corresponds to a rubbery state of the polymer, *i.e.* it is consistent with the maximum value of $\tan\delta$ at the glass transition temperature T_g.

Figure 15 shows the dependence of $\tan\delta$ on D for several copolymers [111] [the D values were calculated using Eqn (48)] for a measurement frequency of 1 kHz. The dependence has clearly defined limits. For $D = 1$, it is extrapolated to $\tan\delta = 0$. When $D = 2$, $\tan\delta$ is roughly equal to the corresponding value at T_g. Thus, linear dependences with the limiting $\tan\delta$ values indicated above can be used to predict the fractal dimension.

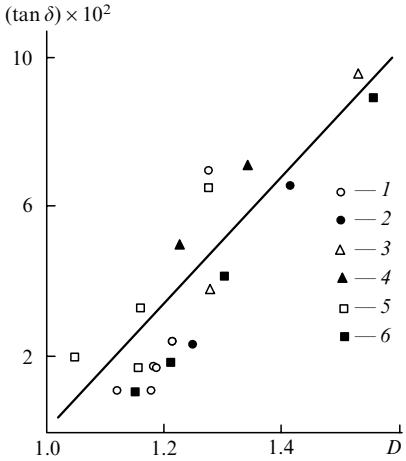


Figure 15. Dielectric loss tangent $\tan\delta$ *vs.* fractal dimension D of the macromolecule section for copolyethersulfoneformals with the content of formal blocks of 0 (*1*), 5 (*2*), 10 (*3*), 30 (*4*), 50 (*5*) and 70 (*6*) mol.%. Measurement frequency 1 kHz.[111]

Now we shall consider examples of using the dimension D for the solution of applied problems. When polymer samples are obtained by solid-phase extrusion, the macroscopic (extrusion) draw ratio λ_e is determined by the ratio [119, 139, 140]

$$\lambda_e = \frac{\varnothing_b^2}{\varnothing_{spin}^2}, \qquad (60)$$

where $\varnothing_b$, $\varnothing_{spin}$ are the diameters of the billet and the spinneret, respectively.

However, the structure and properties of oriented polymers are characterised much more adequately by the molecular draw

ratio λ_{mol}.[122] The following expression relating λ_e, λ_{mol} and D to one another has been obtained:[120]

$$\lambda_{mol} = \frac{l_{st}\lambda_e^{2/D}}{R_s}. \quad (61)$$

It follows from this relation that the lower D, *i.e.* the more 'frozen' the molecular mobility of the chain during drawing, the greater λ_{mol} (the more efficient the orientation process), all other factors being the same.

The limiting draw ratio λ_∞ attained by stretching a polymer is determined, in terms of the rubbery high-elasticity theory, by the equality [121]

$$\lambda_\infty = n_{st}^{1/2}, \quad (62)$$

where n_{st} is the number of statistical segments.

This equation has been applied repeatedly to vitreous polymers. The following fractal relation has been obtained:[38]

$$\lambda_\infty = n_{st}^{D/4}. \quad (63)$$

It can be easily seen that an increase in D for n_{st} = const enhances the deformability of polymers. Equations (62) and (63) are identical when $D = 2$, *i.e.* for rubbers.

An important difference between Eqns (62) and (63) is that in the former, λ_∞ depends on one parameter, which is typical of equilibrium Euclidean objects, while in the latter, it is a function of two parameters, which is typical of thermodynamically nonequilibrium fractal objects. Therefore, the use of Eqn (62) in the latter case is improper.

The relationship between the statistical chain flexibility, characterised by C_∞, and the dimension D has been found [141]

$$D = 2 - \frac{1}{C_\infty}. \quad (64)$$

Using published data for C_∞ (see, for example, Ref. 90) and Eqns (27) and (49), the lengths of chain sections between entanglements L_{en} were calculated. The results were in agreement with experimental data (Table 7). Thus, the increase in the density of the network of macromolecular entanglements following an increase in the statistical chain rigidity was confirmed within the framework of fractal analysis. By combined use of Eqns (27) and (49), one can predict the increase in the number of points of topological fixing of a macromolecule in the vitreous state with respect to the rubbery state.[141]

The fractal dimension D of a chain fragment between the points of topological fixing (entanglements, clusters, cross-links) is an important structural parameter, which controls the molecular mobility and deformability of polymers. Crucial factors accounting for the use of the dimension D are clearly defined limits of variation ($1 < D \leqslant 2$) and dependence on the supermolecular structure of the polymer. It should be emphasised that all fractal relations contain at least two variables. Therefore, correlations between some property of polymers and the density of the network of entanglements (cross-links), which are frequently encountered in the literature, can serve only as illustrations. The necessary use of at least two parameters (for instance, d_s and d_f with a constant d) is a fundamental condition, which follows from the fractality of the intermolecular skeletons in vitreous polymers.

Table 7. Characteristic ratios C_∞ and L_{en}.[131]

Polymer	C_∞ [90, 132]	L_{en}/ nm	
		experiment	calculation
Poly(n-dodecyl methacrylate)	13.4	226	208
Poly(n-octyl methacrylate)	10	177	149
Polystyrene	10	104	149
Poly(vinyl acetate)	9.4	88	136
Poly(n-butyl methacrylate)	9.1	130	131
Poly(methyl methacrylate)	8.6	97	92
Polyethylene	6.8	56	88
Poly(vinyl chloride)	6.7	31	87
Polytetrafluoroethylene	6.3	41	80
Polyamide-6	5.3	46	61
Poly(propylene oxide)	5.1	60	58
Poly(ethylene oxide)	4.2	45	43
Poly(ethylene terephthalate)	4.2	21	36
Polyetherterephthalate	3.3	28	30
Polycarbonate	2.4	29	17

IV. Conclusion

The fractal properties of a macromolecule in a polymer are predetermined by thermodynamic nonequilibrium and by the presence of a certain deterministic order. Proceeding from this fact, we considered the limitations of the scope of the concept of polymer fractal, developed for polymer solutions, and the Vilgis theory for condensed media (melts and rubbers). The major drawback of these approaches is that they neglect the effects of macromolecular entanglements. It is demonstrated that a description of the fractal properties of macromolecules cannot be physically correct without allowance for entanglements. Examples are given to illustrate the diversity of fractality in polymers. In particular, it is shown that not only macromolecular coils but also sections of macromolecules between the points of topological fixing (cross-links, entanglements) are stochastic fractals.

Conditions required for the fractality to be manifested are discussed. They include the range of scales, self-similarity and fractional dimension. It is shown that a section of a macromolecule between the points of topological fixing possesses configurational fractal properties, caused by the mutual arrangement of fragments of the macromolecule, and conformational fractal properties, conditioned by the state of bonds within a section of rigidity (*i.e.* statistical segment). In this connection, a model of structure formation in network polymers is considered; this model includes a quantitative determination of the relationship between the cross-linking density and the level of local order of the structure. It is demonstrated that, in addition to the parameters of local order, fractal dimensions of the polymer structure should also be taken into account. Examples of practical use of the fractal dimension of the section of a macromolecule between chemical cross-linking points are given; it is shown that this value can serve as a measure of molecular mobility. The influence of characteristics of molecular and topological levels of the structure of cross-linked polymers on the fractal dimension is noted.

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