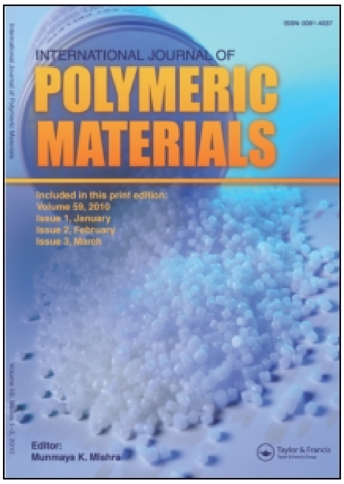

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Twofold Description of the Morphology of Polymers

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Twofold Description of the Morphology of Polymers

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A statistical treatment of the complex morphology of polymeric chains, trees and networks is developed. Its usefulness consists in the possibility to describe intricate properties in terms of a twofold diagram and a very simple correlation function. The method proposed here has been applied in other fields such as: (i) porous media,[1–5] (ii) physical adsorption,[6,7] and (iii) the morphology of products of aggregation and gelation.[8] Firstly, having in mind that the span of applications is very wide, the foundations of the twofold description are stated in a rather abstract form. Subsequently, they are exemplified in some detail for the case of statistical copolymer chains. Finally, a great variety of systems of interest in polymer science in which twofold description is valuable are briefly pointed out.

KEY WORDS Statistics, morphology, polymers, copolymers, trees, networks

FOUNDATIONS OF THE TWOFOLD DESCRIPTION

In order to obtain a convenient statistical description of many complex systems, it is proposed to perform the following steps:

—to decompose the system into a collection of two kinds of interrelated elements, "sites" and "bonds", having a different function in the network that must be clearly established.

—to recognize a "metric", or property such as size, number of repetitive units, energy, etc. that characterizes each element. In order to compare this property between these two kinds of elements, the nature of this metric must be the same for both sites and bonds.

—to point out, from the very definitions of "site" and "bond", a "construction principle": an obvious and constant inequality in metric for each site compared to any of its corresponding bonds. Chains, trees and networks observing this principle are termed "self-consistent".

—to propose a distribution of this metric for each kind of element. The twofold distribution must be set on a number of elements basis and normalized.

—if the distributions of sites and bonds are inappropriate or their overlap is considerable, then the construction principle risks to be violated. In order to avoid this event, two "self-consistency laws" arise: (i) the first law deals with restrictions imposed to the distributions as a whole in order to have a permitted collection of sites and bonds, and (ii) the second law is of a local character and prevents the reunion of elements that could violate the construction principle.

—a balance of sites and bonds when performing a self-consistent assignation of the metric to directly related elements allows to determine readily the function expressing the correlation of metric along the structure. This function is similar for different types of structures.

—when the randomness of this assignation of metric to the elements is raised to a maximum while self-consistency remain the only restriction, the structure is termed "verisimilar", or having the most expected morphology in the absence of other particular informations. Conversely, a confrontation between a verisimilar model and experiment leads to the conviction of physicochemical constraints to randomness in the formation of chains, trees or networks.

—the use of this function, either by analytical (probabilistic) or by digital (Monte Carlo) methods makes evident a "segregation effect" of the metric throughout the structure, i.e. usually they are non-fully random media but there exist regions of reunited elements exhibiting extreme values of the metric.

Thus, the statistical description renders not only a more detailed, because of a dual, distribution of the metric, but also precious information about the morphology, or the sequence of values of the metric along the structure, statistically expressed.

The term "twofold description" is related to the consideration of two kinds of elements, but this treatment can also be multivariated, as for arboreous aggregates.

COPOLYMERS

As an example of application of the quite abstract procedure outlined above, let us consider a linear copolymer formed by type A and B monomeric units as ···-A-B-A-B-B-B-A-A-B-B-B-···. If N_A and N_B are respectively the number of repetitive units of A and B in a given chain, and if $N_S = N_A + N_B$ is the total number of monomers in the chain, it is obvious that, for every chain:

$$\text{CONSTRUCTION PRINCIPLE} \qquad N_S \geqslant N_B \tag{1}$$

Suppose that B is the major component, and that the distributions of N_S and N_B overlap considerably (see Figure 1). If the normalized distribution functions of these quantities are F_S and F_B, then the probabilities to find values of N_S and N_B up to a particular value $\mathbf{N}$ of the metric are, respectively:

$$S(\mathbf{N}) = \int_0^{\mathbf{N}} F_S(N)\, dN; \qquad B(\mathbf{N}) = \int_0^{\mathbf{N}} F_B(N)\, dN \tag{2}$$

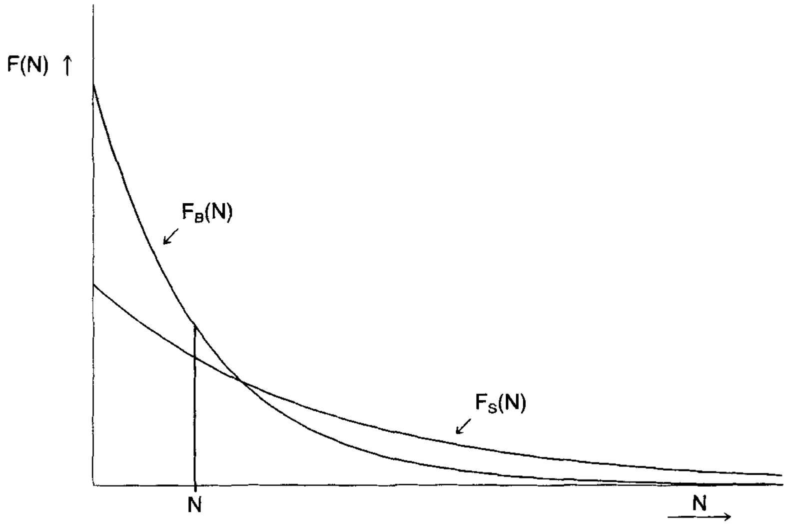

FIGURE 1 Twofold distribution of N_S and N_B.

Overlap means that there can be found a value of N_B higher than some other of N_S. These of course, by virtue of the above condition, do not correspond to the same chain.

Two SELF-CONSISTENCY LAWS must be observed in order to fulfill the construction principle: (i) The FIRST LAW concerns a general relationship between the overall distributions:

$$\text{FIRST LAW} \qquad B(\mathbf{N}) \geqslant S(\mathbf{N}) \qquad \text{for every } \mathbf{N} \tag{3}$$

otherwise the total number of repetitive units, N_S could not be enough important to accommodate in each chain the units of B specified in the number distribution of this own B-element. Thus, each whole chain is playing the role of a site while its content of B-monomers play the role of a bond. (ii) If the probability density $\rho(R_S \cap R_B)$ of the joint event of finding a chain of N_S total monomers and N_B monomers of B in this chain can be expressed as:

$$\rho(N_S \cap N_B) = F_S(N_S)F_B(N_B)\phi(N_S, N_B) \tag{4}$$

where $\phi(N_S, N_B)$ is a function of correlation, then a SECOND LAW holds for each chain in order to avoid the reunion of an inconsistent pair of values of N_S and N_B:

$$\text{SECOND LAW} \qquad \phi(N_S, N_B) = 0 \qquad \text{for } N_S < N_B \tag{5}$$

In order to develop an expression for ϕ in the correct condition $N_S \geqslant N_B$, let us propose a particular method of assignation, to each chain of length N_S, a proper value of N_B.

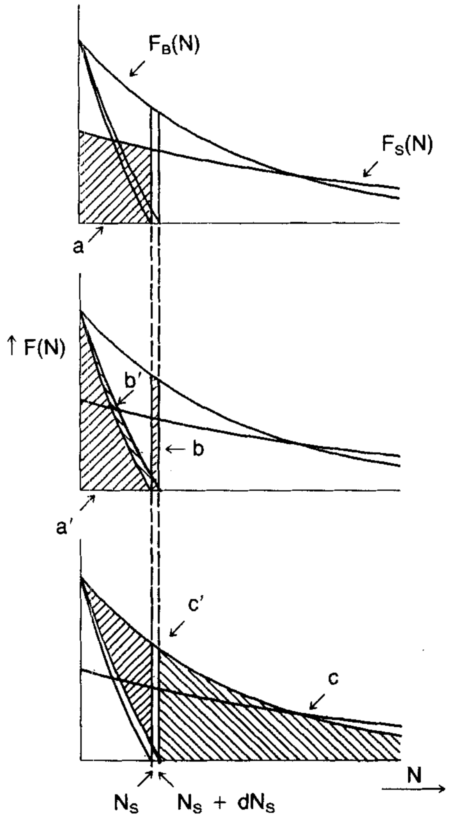

FIGURE 2 The meaning of several quantities appearing in Equations (6)–(9).

This treatment follows very closely these for the deduction of similar functions ϕ playing a role in the topological structuration of porous media and adsorbent surfaces.[1,4,6]

We consider first the smallest chains, and then assign to each of them a value of N_B randomly choosed among the values lower than N_S corresponding to these chains, i.e. with the only restriction indicated by the construction principle, Equation (1). If the first law has been observed, this is always possible.

The procedure follows in such a way as to continue the exhaustion of chains, each time bigger. This method would seem very arbitrary at first sight. This point will be discussed later, when an alternative procedure will be outlined.

An intermediate stage of such process is schematically depicted in Figure 2.

Wasted values of N_B area (a') have already been assigned to chains with lower N_S (area a). Values of N_B smaller than N_S (area b'), randomly chosen from the available distribution (area c') are assigned to chains with length between N_S and $N_S + dN_S$. As the distribution curves are normalized, the following relationships arise:

$$a = a' = S(N_S) \tag{6}$$

$$b = b' = F_S(N_S)\, dN_S = dS(N_S) \tag{7}$$

$$c = 1 - B(N_S) \tag{8}$$

$$c' = B(N_S) - S(N_S) \tag{9}$$

the conditional probability density of finding, for a chain of length N_S, a number of monomers of B equal to N_B is, according to (4):

$$\rho(N_B/N_S) = \rho(N_B \cap N_S)/F_S(N_S) = F_B(N_B)\phi(N_B, N_S) \tag{10}$$

Values of a fixed N_B are progressively exhausted as chains longer and longer (starting with those of N_S equal to N_B) are being suffering assignation. The "exhaustion function", $\mathfrak{F}(N_B, N_S)$ of values N_B being exhausted for chains with length N_S or lower, grows differentially along the process of assignation according to two factors: (i) the fraction of new chains, $dS(N_S)$ and (ii) provided these chains have in fact N_B monomers of B, $\rho(N_B/N_S)$:

$$d\mathfrak{F}(N_B, N_S) = \rho(N_B/N_S)\, dS(N_S) = F_B(N_B)\phi(N_B, N_S)\, dS(N_S) \tag{11}$$

The construction principle may be expressed, taking into account the restriction imposed by Equation (5) as:

$$\int_o^{N_S} \phi(N_B, N_S)F_B(N_B)\, dN_B = 1 \tag{12}$$

b', the fraction of exhausted N_B of all permitted values when chains of length between N_S and $N_S + dN_S$ are assigned is obtained by performing an integration along N_B while keeping N_S constant. From (11) and (12) we obtain:

$$b' = \int_0^{N_S} d\mathfrak{F}\, dN_B = dS(N_S) \tag{13}$$

During a differential step of assignation, the ratio between the fraction $d\mathfrak{F}\, dN_B$ (all of specific value N_B), and the total fraction of values of N_B, $dS(N_S)$ (allowing for all the possible N_B values), both assigned to chains of length N_S, is equal to the ratio between available specific values N_B (those which have not yet been assigned to any site), $[F_B(N_B) - \mathfrak{F}(N_B, N_S)]\, dN_S$, and the fraction of all the available possible values N_B (those not yet been assigned and corresponding to a span of N values between zero and N_S), $B(N_S) - S(N_S)$:

$$\frac{d\mathfrak{F}(N_B, N_S)}{dS(N_S)} = \frac{F_B(N_B) - \mathfrak{F}(N_B, N_S)}{B(N_S) - S(N_S)} \tag{14}$$

This expression can be integrated, while keeping N_B constant, between the following limits: at the start of the assignment of values N_B, we deal with chains such that $N_S = N_B$ and $\mathfrak{F} = 0$, while the assignment proceeds to any point characterized by the conditions $N_S > N_B$ and $0 < \mathfrak{F} < F_B(N_B)$. Since N_B has been kept constant, $F_B(N_B)$ also adopts a fixed value. Then, the integration yields:

$$\mathfrak{F}(N_B, N_S) = F_B(N_B)\left[1 - \exp\left(-\int_{S(N_B)}^{S(N_S)} \frac{dS}{B - S}\right)\right] \tag{15}$$

From Equations (11), (14) and (15), the final expression for ϕ is obtained:

$$\phi(N_S, N_B) = \frac{\exp\left(-\int_{S(N_B)}^{S(N_S)} \frac{dS}{B - S}\right)}{B(N_S) - S(N_S)} \tag{16}$$

Had the bonds been taken from the larger to the smaller ones, while applying in each case the proper site sizes (randomly but still respecting the construction principle), this inverse procedure would lead to the completely equivalent expression for ϕ:

$$\phi(N_B, N_S) = \frac{\exp\left(-\int_{B(N_B)}^{B(N_S)} \frac{dB}{B - S}\right)}{B(N_B) - S(N_B)} \tag{17}$$

If the function ϕ were always equal to unity for any pair of values of N_B and N_S, the events of finding a chain of a given length and a given number of B monomers for it would be independent [cf. Equation (4)], and in this case the assignation of values of N_S and N_B to the chains should be totally at random. This can occur only when the overlap between the corresponding distributions is zero. Conversely, $\phi \neq 1$ means that these values are correlated.

Since the equivalent expressions (16) and (17) for the function ϕ have been obtained raising the randomness to its maximum permitted degree, this stoichiometric model can be termed Verisimilar, i.e. that corresponding to the minimum number of constraints (the construction principle being the only restriction introduced), or that which is the most expected to correspond to a real system in the absence of other information (additional constraints) about the particular physicochemical nature of the composition of the mixture related to the kinetics and mechanism of its preparation or any other relevant aspect of it. Some kinds of constraints that could affect the former expressions are mentioned elsewhere.[4,6]

Suppose that all of the polymeric chains bear some kind of additional restriction, e.g. all of them contain a minimum number, α, of the monomer A as a result for example of an incorporation of α-sized blocks of A. The function of correlation takes the form:

$$\phi(N_S, N_B) = \frac{\exp\left(-\int_{S(N_B+\alpha)}^{S(N_S)} \frac{dS(N)}{B(N - \alpha) - S(N)}\right)}{B(N_S - \alpha) - S(N_S)} \tag{18}$$

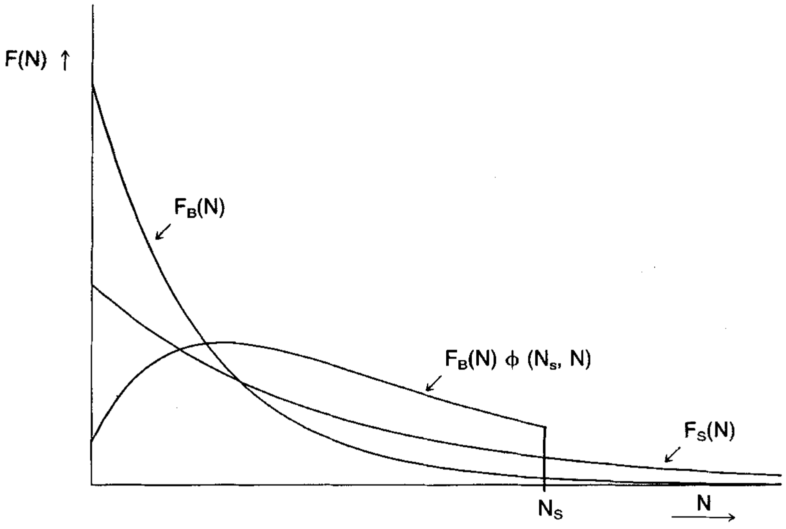

FIGURE 3 $F_B\,\phi$, the distribution of the number of B monomers for a particular value of N_S.

Similarly other particularities, acting as additional restrictions, could be expressed as modifications of ϕ.

Analysis and confrontation of experimental (NMR) results of r-mers and kinetic schemes with this treatment could be very useful in order to make evident several kinds of effects or tendencies as well as to describe a complex system in a simple form.

In consequence, for a chain of a certain total number of repetitive units N_S, the conditional probability density to find N_B is:

$$\rho(N_B/N_S) = F_B(N_B)\phi(N_S, N_B) \tag{19}$$

Thus, this particular form of ϕ allows, in the case of a fully-random distribution of monomers A and B, a direct and readily way to calculate the distribution of composition of chains according to their size (see Figure 3).

The treatment is straightforwardly applied to deal with the distribution of dimers, trimers, etc. for a given length of the chain. In general scarce monomeric units, whose distributions do not overlap with the site distribution, are fully-random organized, while frequently encountered species are allocated in chains in a correlated way. Several species distributions could be simultaneously correlated with the length of the chain.

OTHER APPLICATIONS

Arboreous Aggregates

These structures are the result of diffusion-limited aggregation, from a central seed, of particles endowed of brownian motion. They can be readily decomposed in chains of n elements (primary aggregate particles), from which other chains develop. Successive levels of order can be distinguished: Starting from seed particle, there develop first-order chains, which possess the greatest number of particles, and from them there appear second-order chains, etc. In dealing with neighboring-order chains, the ancestor can be termed "stem" while their descendents are "branches". Now, if this classification is adopted, higher-order chains have always a smaller number of elements than their own lower-order ancestors. The position of branching BS (branch seed) with respect to the end of the ancestor SB (stem boundary) is very important.

From the very definitions of "stem" and "branch", it follows the construction principle of the whole structure: "The number of elements of a branch is always smaller or at most equal to the number of elements from the branch seed up to the stem boundary," so that stems play the role of sites while branches are bonds. A very important step of this treatment consists in performing a transformation from the distribution of n_S to the distribution of $n_{BS \to SB}$, which is the quantity directly involved in the construction principle.

It is worth pointing out that in this treatment all the elements located at the same number of particles up to the last particle SB of their stem possess the same probability density to generate a branch of a given size n_B, no matter the value n_S of their own stem.

A segregation effect arises. This phenomenon is evident and consists in that for a certain stem, the branches are more important the closer they are to the seed, just as a pine tree. Also, "long" stems have a tendency to be ancestor of "long" branches.

It is possible to generate interesting fractals, as they are in the sense that the same kind of metrics, in this case the convolution properties of the neighboring-order chain distributions as well as the connectivity (the average ratio of number of seeds SB of a stem to the number of elements n_S of the same stem), is conserved from one change of stem order to the other. Again, the method leads to describe complex structures in very simple terms. It allows also to generate verisimilar morphologies that can be compared with results of transmission electron microscopy or Monte Carlo calculations of DLA aggregation in order to account for physicochemical preferences during the formation of aggregates.

This approach coould also be applied to graft, cross-linked and other sort of ramified polymers.

Dense Aggregates

The clearest example could be related to silica aggregates, in which particles of about the same size are joined together during gel formation. After a certain degree of sinterization, there remains a network constituted by alternated elements: "sites" (solid bulges, solid globules or their remains) and "bonds" (solid bridges between globules, minima in the cross-section of the solid phase).

Porous Networks

These are the counterpart of the systems mentioned immediately above. They are extensively described elsewhere.[1–5] The size of a site (antrum, cavity) can be approximated to the radius of the inscribed sphere inside the hole, while the size of a bond (passage, window) is related to the radius of the inscribed circle of the minimum cross-section defining this bond. If all sites are considerably larger than all of the bonds, their distributions are not overlapping. The size topology of sites and bonds can exhibit a totally random character, since the construction principle could never be violated in this case. As overlap between distributions becomes considerable, i.e. many sites have R values smaller than those of certain bonds (these bonds of course cannot be the delimiting ones of such sites), there arise size-correlations between the elements leading to a size segregation effect, the reunion of elements of similar sizes. Finally, when overlap is nearly complete, there appear "homottatic" domains in such ways that the size values for both sites and bonds within each one of the homogeneous domains become the same.

Foams

One important case of the combination of solid and void matrices arises in the description of foams, e.g. polyurethane foams. Quadrifold distributions, two for the solid and two for the void spaces are required.

Cyclic Structures

The treatment becomes still more interesting when another property of networks is considered: The connectivity, or number of bonds delimiting a site. By virtue of the application of the construction principle to structures bearing diverse values of the connectivity for each one of their sites, it can arise a "connectivity segregation effect" which consists in that there form regions of higher connectivity and bigger elements, and other ones of low both connectivity and elements size. Truncated spherulites seem to suffer these combined effects. On the other hand glass, an inorganic polymer, that has been represented in two dimensions by the Zachariassen model, possess rings constituted of siloxane elements joined cyclically. The size of the site is represented by the variable-number of oxygen atoms of the ring, while the bonds or Si—O—Si bridges delimiting one site from another are all equal. No overlap of distributions is possible in this case, so that glass seems to be a totally disordered structure, in which neighboring sites are by no means correlated.

CONCLUSIONS

The twofold description has been previously applied to study complex structures in several fields. It was shown here that this method can be equally useful to describe polymer morphologies.

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