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Chain overlap and intersegmental interactions in polymer solutions*

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A combinatorial analysis of solution structure is presented and kinetics of the polymer dissolution process considered. Equations relating the extent of chain overlap to polymer concentration c are derived. The relations allow better management of solution processing of polymeric materials as well as improved drag reduction. Current definitions of the critical concentration c^* separating dilute solutions from semidilute ones are examined. We find that overlap does occur at c values distinctly lower than c^*. As a corollary, regions in solution which do not contain any polymer chains occur also when $c > c^*$. A number of experimental findings reported in the literature can now be explained.

(Keywords: polymer solutions; chain overlap; solution structure; liquid flow; drag reduction; polymer solution processing; macromolecular conformations)

Introduction

Properties of polymer solutions are strongly dependent on the polymer concentration c. This communication provides a procedure for computing the extent of chain overlap which is particularly important. Polymer solutions are usually divided into three categories as a function of c: dilute, semidilute and concentrated[1]. Expressing c in mass per volume:

$$O < c_{\text{dilute}} \leqslant c^* < c_{\text{semidilute}} < c^{\neq} < c_{\text{concentrated}} \quad (1)$$

The term $c^{\neq}$ has been defined in various ways[1,2] as a function of c^*; hence a correct definition of c^* is essential. However, although c^* has been extensively used, there is a variety of definitions for this quantity, many of them mutually incompatible. To make matters worse, some experimental findings contradict all extant definitions. Fortunately, the procedure of computing the average degree of overlap for given c presented below also provides a new interpretation of the physical significance of c^*—one which agrees with experimental findings.

A widely used definition of c^* reads

$$c^* = M/N_A R^3 \quad (2)$$

where M is the polymer molecular weight averaged for polydisperse systems, N_A is the Avogadro constant and R is the radius of the molecular domain of a single chain. In turn, R can be related to the radius of gyration or to the mean-square end-to-end distance. Alternatively, c^* is defined by

$$V(c^*) = N_2 v_h \quad (3)$$

where V is the total volume of solution, N_2 the number of polymer chains and v_h the hydrodynamic volume pervaded by a single chain. Taking into account the excluded volume, one can relate R^3 and v_h but more than one such relation is in use[3,4]—even for solutions of one polymer in one solvent. In binary mixed solvents v_h

depends on the enthalpy of mixing of the solvent components[5]. Further, Brown and Mortensen[2] concluded from their quasi-elastic light scattering and small-angle neutron scattering experiments that $c^* = 1/[\eta]$; here $[\eta]$ is the intrinsic viscosity discussed for instance by Rabek[6]. That conclusion was used by Brown and Pu[7] who worked with the reduced concentration c/c^*. Graessley[8] derived a formula based on an analogue of our equation (2) but with a factor $6^{3/2}/8$ on the right-hand side; he used the Fox–Flory equation[9] and obtained $c^* = 0.77/[\eta]$. Without that factor the Graessley derivation would give $c^* = 0.42/[\eta]$. Moreover, a claim was made[10] that another critical concentration $c^{**} < c^*$ exists. The situation is still compounded further by reports of the formation of ordered or aggregated structures, in concentrated[11] as well as in dilute[12–17] solutions. In fact, a procedure for computer simulation of the particle scattering factor was developed[13] so as to explain experimental light scattering curves as a function of the scattering angle which exhibited maxima. Simulations have shown that maxima occur when two branched macromolecular chains act as *a single scatterer*.

One can also determine c^*_{LS}, i.e. c^* from light scattering by polymer solutions. However, Kulicke[18] has shown that c^*_{LS} and $c^*_{[\eta]}$ from viscosity determination differ approximately by an order of magnitude.

Definitions (2) and (3) are based on the following considerations. Polymer chains are continually added to a liquid and each chain pervades a volume equal to v_h, creating for itself something like a cell. When the critical concentration c^* is reached, we have the situation depicted in *Figure 1*; there is no empty space but no overlap of chains occurs. Above c^* there are no empty spaces but now overlap takes place; one assumes that the solution properties will then be different. However, a variety of experimental results[7,15,19] shows that no significant changes in solution properties occur at c^*. Alternatively, changes seem to appear at different concentrations for different properties. To evaluate the validity of the prevailing concept shown in *Figure 1* and also to derive the required relationships we shall now employ methods of combinatorics.

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* Dedicated to Professor Dr Hans-Henning Kausch-Blecken von Schmeling on his 60th birthday

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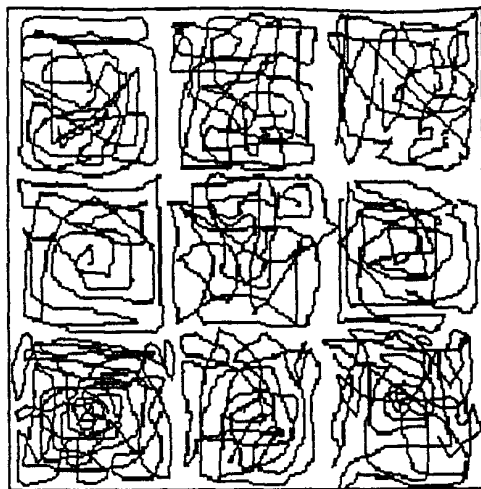
Figure 1 Distribution of polymer chains in solution at the critical concentration c^* corresponding to the hitherto prevailing model. See also *Figure 2a*
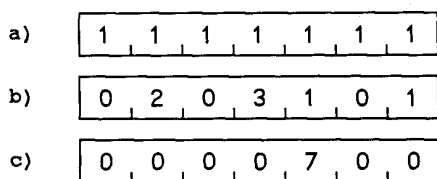

Figure 2 Three sets of occupation numbers $\{n_i\}$ for a system of seven cells at the critical concentration c^*: (a) and (c) represent the extreme cases; (b) is an example which belongs to the most highly populated subclass of combinations

Combinatorics of chain overlap

Consider a system at $c = c^*$. For clarity we consider first an example of a small subsystem: volume $v = 7v_h$; the number of chains = the number of cells. We represent the subsystem by a linear sequence of cells. Each cell is assigned an occupation number n_i where the index refers to the ith cell. The occupation numbers are considered to be integers: when a partial overlap of $< 50\%$ occurs, the overlapping molecule does not contribute to the count, while for $\geqslant 50\%$ it does. *Figure 2a* shows the subsystem in the configuration corresponding to the prevailing concept, i.e. the same as in *Figure 1*, with all occupation numbers equal to unity. However, that configuration is only one of many. In general, the number of combinations with repetition (see e.g. Section 2.3 of ref. 20) of f molecules among z cells is

$$C_{z+f-1}^{f} = (z + f - 1)!/[f!(z - 1)!] \qquad (4)$$

Since in the subsystem under consideration $f = z = 7$, from equation (4) the total number of combinations is 1716. Hence, without any consideration of the process of solution formation, the probability of the only combination in which the chain overlap does *not* occur is 1/1716.

At the opposite end of the spectrum we have combinations of the kind presented in *Figure 2c*: interpenetration of all macromolecules present, in the case under consideration with $n_5 = 7$ and $n_i = 0$ for all other cells; clearly we have seven such combinations. We now define the local degree of overlap σ_1 by

$$\sigma_i = n_i - 1 \qquad (5)$$

The average degree of overlap $\bar{\sigma}$ per system (or subsystem) can be obtained by averaging over non-empty cells in all combinations. A class of combinations corresponds to a given number of empty cells z_e. A subclass contains a specified set of occupation numbers $\{n_i\}$ represented by a sum. For instance for $z_e = 4$ one such set is $5 + 1 + 1$; the order is unimportant. We now need to evaluate the numbers of all possible subclasses. From combinatorics we derive the number of combinations in a given subclass $\Omega(n_1 + n_2 + \cdots + n_z)$ as

$$\Omega(n_1 + n_2 + \cdots + n_z)$$
$$= \{z!/[(z - z_e)!z_e!]\}(z - z_e)! \Big/ \prod_j m_j! \qquad (6)$$

where the product $\prod_j$ extends over all multiple appearances of occupation numbers n_i while m_j is one of such numbers of multiple appearances of an occupation number. Clearly $n_1 + n_2 + \cdots + n_z = f$, and f in conjunction with z determines the polymer concentration.

Calculations and results

For a given value of c we can use equation (6) to calculate the number of combinations for all possible subclasses of a given class, and obtain therefrom $\bar{\sigma}$. Results for the example defined above are listed in *Table 1*. A configuration belonging to the most numerous subclass, with the occupation number set $3 + 2 + 1 + 1$, is shown in *Figure 2b*.

The average degree of overlap obtained from the data in *Table 1* is

$$\bar{\sigma}(c^*) = 1.00 \qquad (7)$$

Similar combinatorial computations for other collections of cells with $z = f > 7$ yield analogous results. In other words, the result is general and valid for the entire system; it does not depend on the size of the subsystem studied. Equation (7) is vastly different from $\bar{\sigma}(c^*) = 0$ for the prevailing model shown in *Figure 1*. It is evident that the chain overlap exists not only at $c = c^*$ but must take place also at $c < c^*$. Detailed calculations of the concentration dependence of $\bar{\sigma}$ will be reported elsewhere.

At the same time, we infer from sets of occupation numbers such as shown in *Figure 2b* and from *Table 1* that even when $c > c^*$ there must be regions in the solution which do not contain polymer chains at all. To

Table 1 Occupation numbers, combinations and the degrees of overlap at the critical concentration c^*

z_e	Set of occupation numbers	Number of combinations Ω in subclass	σ
6	7	7	6.00
5	6 + 1	42	5/2
5	5 + 2	42	5/2
5	4 + 3	42	5/2
4	5 + 1 + 1	105	4/3
4	4 + 2 + 1	210	4/3
4	3 + 2 + 2	105	4/3
4	3 + 3 + 1	105	4/3
3	4 + 1 + 1 + 1	140	3/4
3	3 + 2 + 1 + 1	420	3/4
3	2 + 2 + 2 + 1	140	3/4
2	3 + 1 + 1 + 1 + 1	105	2/5
2	2 + 2 + 1 + 1 + 1	210	2/5
1	2 + 1 + 1 + 1 + 1 + 1	42	1/6
0	1 + 1 + 1 + 1 + 1 + 1 + 1	1	0

	Example	Ω	σ
a)	0 5 0 0 1 0 0	42	4.00
b)	8 6 0 0 0 2 0	42	4.00
c)	0 6 7 3 0 0 0	42	4.00
d)	0 6 0 6 0 4 0	42	4.00
e)	0 5 0 0 0 0 5	21	4.00

Figure 3 Class of combinations with $z = 7$, $f = 10$ (hence $c = 1.429c^*$) and $z_e = 5$. Examples, occupation numbers Ω and degrees of overlap σ for a subclasses

explore this further, consider a different example: $z = 7$ and $v = 7v_h$ a before, but now $f = 10$. The total number of combinations from equation (4) is now 8008. We have, of course, seven combinations when all chains overlap, $z_e = 6$ and $\sigma = 3.00$. Consider now in some detail the class of combinations for which $z_e = 5$. In *Figure 3* we show for each set (subclass) of occupation numbers: one example, in the format already used in *Figure 2*; the number of combinations in a given subclass calculated from equation (6); and the degree of overlap σ. Actually σ has a common value in a given class (*Table 1*), but the averaging which leads to it is different in each subclass, and *Figure 3* demonstrates this fact. The total number of combinations for $z_e = 5$ is 189 which constitutes 2.36% of all possible combinations. There are more combinations for $z_e = 4$ and 3. We infer that there are significant empty regions even when $c > c^*$.

Strictly speaking, our results are valid for θ conditions, when the polymer + solvent interaction is exactly compensated by the influence of volume exclusion[9]. However, when moving away from the θ solvent and with the forces of attraction 'switched on', the solution structure does not change in any significant way[21]. Similarly, for reasonable values of the attractive energy, the end-to-end distance does not change with the chain length[22].

Consider now kinetics of the solution formation, or of dissolution of chains. One starts with a piece of solid polymer, with chains well entangled. Let us take a good solvent first: polymer + solvent interactions are strong relative to those of the polymer + polymer type. However, there is no demon (which would need to have capabilities somewhat similar to the Maxwell demon ...) that could destroy the entanglements, separate all the chains completely and create the combination depicted in *Figure 1*. In poor solvents the tendency to separate the chains for energetic reasons does not even exist. In multicomponent polymer solutions there is a possibility of interpolymer associations[23]. Except for electrolyte solutions with strong repulsive forces, these factors should lead to overlaps even higher than those resulting from our combinatorial calculations.

In a series of papers one of us has shown[24-27] the importance of distinction between internal (both segments on the same chain) and intermolecular contacts (segments from two different overlapping chains). Other authors including Tsvetkov and Lezov[28] also studied the consequences of chain overlap. The distinction between the two kinds of contacts made in references 24–27

enabled an interpretation of experimental results such as the molecular mass dependence of the second osmotic virial coefficient. For polymers in poor solvents that distinction turned out to be indispensable. Important for the interpretations in references 24–27 is the parameter $p^{)(}$, the probability that two contacting segments belong to different molecules. Our results explain how the overlap occurs, while $p^{)(}$ introduced in reference 25 is connected to our $\bar{\sigma}$.

The phenomenon of drag reduction (DR) by polymer additives introduced into flowing liquids has a number of important practical applications including accelerated oil flow in pipelines[29], fire fighting, slurry transport, irrigation (enlargement of irrigated areas), improving capacities of storm sewers[30], fuel misting inhibition, and navigation (increasing the speed of a ship or a boat by installation of a DR releasing agent at the bow). The consequences of the fact that DR takes place in human and animal blood for the amount of food needed for the world's population have been pointed out[31]. Extensive investigations of DR are being conducted, notably by Zakin and his colleagues[32-34], Nguyen and Kausch[35-37] and Bewersdorff and collaborators[38-42]. A model of DR was developed[31] and then extended to binary drag reducing agents[43]. Essential to the model is the elucidation of polymer + solvent interactions and their relative strength in comparison to polymer + polymer interactions. DR occurs often in highly dilute solutions (with concentrations defined in ppm). However, some experimental findings pertaining to DR can only be explained by assuming chain overlap. This applies to the effects of NaCl on DR in polyacrylic acid solutions observed by Kim et al.[44] and ascribed to what they called interchain association. The same group had observed a DR increase with shearing[45]—explained[43] by a decrease in chain overlap produced by deformation. We know that deformation of flowing units produces changes in their interactions[46], while the flow itself causes deformations with respect to the solution at rest. Now, *Table 1* and equation (7) show us how much chain overlap exists at c^*. Evidently, even when DR takes place in highly dilute solutions, the overlap has to occur there also.

Our results enable better management of some industrial processes and also explanations of a variety of experimental findings which hitherto were hard to elucidate. For instance, curves of η_{sp}/c versus c, where η_{sp} is the specific viscosity, determined by Dondos et al.[10] show changes of slope at $c^{**} < c^*$. While c^* values are not provided, it is at least possible that around c^{**} the chain overlap begins to manifest itself. Continuity of solution properties around c^* reported by a number of experimentalists, often rather circumspectly, now acquires a clear explanation. Chain aggregation in dilute solutions[12-17] can be viewed as a simple manifestation of the chain overlap. The critical concentration c^* does have a physical significance—albeit different than previously supposed. Equation (7) can be used to define c^*.

It is curious why, in spite of such a wide use of c^*, its correct physical significance given by equation (7) was not established earlier. It appears that in a number of cases c^* has been applied simply as a reducing parameter. The same is true for $[\eta]$ and for multiples of $[\eta]$. Dimensionless quantities of the general form $\bar{N} = N/N^*$,

where N^* is a reducing parameter, are quite convenient to use; this has been the case here also.

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