THERMOKINETICS OF FORMATION OF ORDERED STRUCTURES IN POLYMER SOLUTIONS AND GELS

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ABSTRACT

A general approach is proposed allowing the reduction to a 'common denominator' of different forms of formation of ordered structures in polymer–solvent systems. This 'common denominator' results from the combination of the equivalence principle of thermokinetics and the concept of diphility of macromolecules. In the first sections the discussion deals with a precise definition of order and with the foundation of the equivalence principle and related physical formalisms.

It is shown that the consideration of any mode of structure formation can be reduced to the analysis of phase diagrams and free energy–temperature diagrams, the possibility of such reductions being connected with two main assumptions (supported by all known experimental data):

(*i*) Due to inherent diphility the Flory–Huggins parameter χ_1 can change continuously or discontinuously with the concentration of components leading to the occurrence of preferential chain conformations or abrupt intramolecular conformational transitions. In cases of pronounced explicit diphility (in random or block copolymers) the preference of interactions also leads to intramolecular segregation which on increasing polymer concentration develops as a supermolecular order.

(*ii*) One can connect these conformational transformations with the dependence of Flory's flexibility parameter f on χ_1. Taking into account this dependence makes it possible to interpret identically 'antiplastification' phenomena, the formation of liquid crystalline mesophases with different morphologies and the formation of binary crystals.

Hence, various manifestations of molecular and supermolecular forms of ordering in solutions and gels can be treated by analogy with the usual polymorphism in polymers, in the same way as in the Flory–Mandelkern crystallization theory.

The equivalence principle allows us to consider from quite similar positions the nucleation and growth of crystals or liquid crystals in the presence of external fields. In these cases the flexibility parameter f turns out to be dependent on the external field and all further considerations can be reduced to the already analysed situation with variable and interdependent χ_1 and f parameters. A more profound analysis shows that this equivalence is not formal but reflects the real state of events. The uncoiling of macromolecules in a shear or longitudinal field and the increase of their interactions means in reality the increase of the interaction parameter χ_1 and ultimately the loss of solubility, or desolvation.

The analysis from those positions of a large amount of experimental data shows that in some cases organized structures may exist only in the presence of a

solvent which stabilizes them thermodynamically rather than only stimulates kinetically their formation.

When organized structures are formed due to external fields they can persist on the elimination of the field and removal of the solvent, on condition that the energy 'pumped over' in the system from the external field is compensated for as the latent crystallization heat (i.e. is simply used for crystallization in the strict sense of the word). In the opposite case (in an atactic polymer) the oriented state is unstable due to developing internal stresses. In special cases these stresses lead to an 'orientational catastrophe'—the self-annihilation of the sample.

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1 INTRODUCTORY NOTES

1.1 On the concept of order in polymers

Before summarizing the different data presented at this Symposium one must try to make some general statements about what we understand as 'order' in polymer–solvent systems. This is necessary not only to avoid possible confusion and misunderstanding but also to limit oneself to the discussion of the most realistic and important (or, maybe, typical) cases of ordered structures formation.

Probably the first limitation must be connected with the *range* of order. Although in discussing molecular and supermolecular order in polymers many authors include in the definition of order *short range* order, for instance in amorphous polymers, this does not seem to be correct or in accord with the general principles of molecular physics. Of course the appearance of short range order in the liquid state is a necessary step in the transition from the total disorder presented by the gaseous state to a total order which is attainable only in cases of covalent crystals of the diamond type (which immediately returns us to polymers, the non-covalent simple molecular crystals being always imperfect!). On the other hand, one still makes a distinction between ordered and unordered simple liquids, for instance liquid crystals and isotropic liquids, some anisotropic liquids being intermediates within the liquid state, which is an intermediate state itself.

Thus both everyday logic and a need for correct formulations lead us to the *long range order* as a 'representative of Order' in polymer–solvent systems. These didactic problems that I have mentioned very superficially are of the same kind as the problem of comparison of liquids with gases and/or solids[1]. In the case of polymers an additional peculiarity, both physical and didactic, immediately arises, the polymer chains *per se* (even atactic) presenting a sort of unidimensional order the range of which is determined by the degree of polymerization. However, if we adopt Huggins's struction concept[2] to describe not only the molecular but also the supermolecular mode of distribution of chain units in space, then most difficulties can be avoided, and we come back to the definition of order as some kind of long range packing, the structons being formed by repeating units, chain segments or, in some cases, by the whole macromolecules. Here, by 'packing' we denote only the type of spatial distribution of characteristic units, without further limitations concerning immobilization, or mode of thermal motion, or closeness (of packing) etc.

The given definition of order includes three-dimensional crystalline lattices

as well as systems with only lateral or only longitudinal (or both) long range order. Thus, it includes automatically every kind of liquid crystalline mesophase. In addition—and this is important—one can take into account *different levels* of order, the role of 'elementary units' being played in those cases by crystallites, fibrils or other morphoses having a sufficient amount of *internal* long range order. Such an approach will lead us to the concept of structons of 'higher ranges' which coincides in sense with Hosemann's paracrystalline concept of matter[3].

Two more words should be written about the magnitude of structural units that we still are allowed to call ordered. Just as in the case of heterophase fluctuations[1] existing in equilibrium with the main phase, one should start with stable crystallization nuclei which for some reason or other cannot grow. polyvinyl alcohol in water giving a most striking example of such behaviour. One can treat these nuclei as 'frozen' heterophase fluctuations, and later we shall discuss their nature in some detail.

As to the linear dimensions of these minimal ordered units, the criterion of order will be connected only with the possibility or impossibility of checking the presence of order by means of x-ray or electron diffraction.

1.2   The thermokinetic approach

By thermokinetics I mean the physical kinetics of phase transitions and changes in order of polymer systems. However, the term by itself hints at some kind of hybridization of thermodynamics and physical (and in some cases also chemical) kinetics. One can alternatively define thermokinetics as a form of statistical mechanics where the partition function and all the related values are treated from the *structural* point of view. Correspondingly, one must consider the time derivatives of the partition function or other time-dependent external or internal parameters, for in reality there exist no physical structures that can change instantaneously.

Thus the mentioned time derivatives of the partition function (and consequently of free energy, entropy, etc.) and other time dependent factors must figure explicitly in the equations describing phase transitions, changes in phase equilibria and in general any changes in any systems under the influence of any kind of external fields. In this sense thermokinetics is not 'tied' specially to polymer systems. However, if for ordinary systems (as for instance in the kinetic theory of gases) these time-dependent factors play a part of only small corrections that can be usually neglected, in polymer systems these 'corrections' may turn out to be the dominating factors defining both the character of the transition and the morphology (and related properties) of the resulting state.

Thus, I try to advance a concept rather than a new term. The source of this concept can be found in the *Kinetic theory of liquids*[1], the kinetic theory of phase transitions being a specific part of the general theory.

The thermokinetic approach to polymer systems as an extension of the above mentioned theory to any kind of structural changes was first proved by the author and G. K. Elyashevich in two papers[4, 5] where the necessary details can be found. In what follows the same approach will be used to discuss some typical cases of formation of order in polymer solutions and gels.

It should be added that some of the confusion concerning the phase

transitions in polymers is largely due to the fact, usually neglected, that polymerization itself is a very specific and fundamental phase transition involving at least three groups of symmetry, namely those of translations, rotations and reflections[6]. All physical changes in a polymeric system proceed so to say on a background of this already completed 'main' transition. Thus, in some instances they are not sufficiently pronounced and as a result are mistreated, and in some other cases critical effects appear where they should not be present if we try to apply for polymeric systems the laws derived for simple bodies[7-9]. Though this is still a point of discussion, in my opinion most contradictions connected with the nature and/or order of phase (and other, for instance glass) transitions in polymers are due to the same neglect of the phase nature of polymerization.

To make the following description more illustrative I shall use diagrammatic representations rather than formulae. The axiomatics of thermokinetics allows different formalisms, the most suitable of them (for the problem under discussion) being the 'deformation of phase diagrams', the latter presented by the coexistence or free energy–temperature curves. In further sections we shall show the application of this formalism to concrete examples.

2 THERMODYNAMIC AND KINETIC STABILITY OF AQUEOUS POLYVINYL ALCOHOL SOLUTIONS AND NON-GROWING STABLE CRYSTALLIZATION NUCLEI

The coexistence curve for PVA–water systems has been a subject of controversy for a long time. The main experimental difficulty was the practical impossibility of obtaining even at high dilutions, a purely stable solution at appropriate temperatures. Always after some time colloid 'gel-particles' were generated, the process being quite similar to that of amylose retrogradation. Filtration or centrifugation does not allow us to eliminate these particles: after some time new ones are generated. On the other hand, at some sufficiently high concentrations, for instance in spinning solutions, and consequently at sufficiently high viscosities one still can obtain a fairly stable state without gelation or formation of microgels for an appropriately long time.

The problem was discussed in detail by the Saratov group (Klenin et al.) in a series of studies where turbidity spectra, light scattering and electron microscopy were used as main methods of observation[10,11]. The main results of these studies can be summarized as follows.

The second virial coefficient A_2 of cleared and gel-particle-free solutions of PVA decreases with increasing temperature, the extrapolation pointing to a 'reversed' (Rowlinson) Θ-temperature near 160°C. However, direct measurements (for experimental details see Refs. 10–11) show that at temperatures close to 130°C, A_2 starts to increase again. Thus one must conclude that the PVA–water systems are represented by a superposition of binodals leading to the so-called 'flower vessel like' phase diagram (*Figure 1*). This does not explain, however, the generation of gel-particles in the would-be stable region on the left side of the diagram at room or even elevated temperatures. The only possible explanation is that in the whole attainable concentration range the equilibrium melting temperature is higher than 100°C.
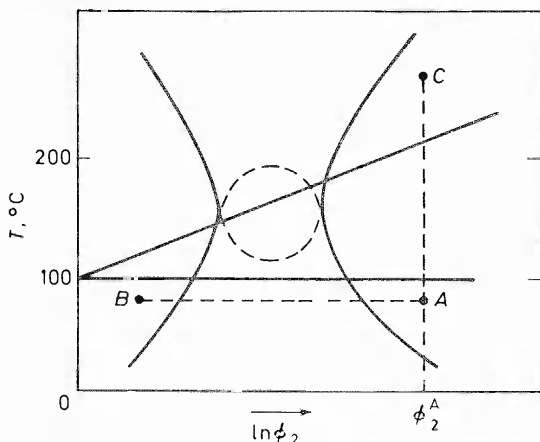
Figure 1. The coexistence diagram PVA–water. The ordinary and 'inverted' binodals overlap. The thick line represents the dependence of the melting temperature on concentration. On the abscissa the logarithm of concentration is plotted in order to compensate for the usual strong skewness of phase diagrams of polymers

Then a continuous nucleation is unavoidable: however, two new questions arise: (1) why this nucleation does not lead to formation of lamellar single crystals or spherulites? and (2) why at higher concentrations no crystallization occurs?

To answer the first question one must introduce the notion of inherent diphility which applies not only to PVA. (It should be kept in mind that we discuss here the behaviour of a sufficiently pure PVA only, containing less than 1 per cent of acetate groups). The concept of inherent diphility has the same physical meaning as the concept of diphility, or amphiphility in the case of copolymers. For instance, in the case under consideration there is a kind of 'conflict' between the non-polar backbone of the PVA chain and the polar side OH-groups. This 'conflict' is amplified in the presence of water, the backbone trying to attain a supercoiled conformation. Of course such a conformation does not favour the evolution of crystalline growth, the crystallization being terminated henceforth at the nucleation step, but the nuclei remaining stable in the same way as micelles. The size of these nuclei is sufficiently large to make them observable by x-ray diffraction. As was shown in our work with Baranov and Volkov[12], as well as in some earlier Japanese work (see Ref. 12), one can eliminate the effects of inherent diphility by the use of suitable solvents modelling to some extent the structure of short parts of the PVA chain. For example, it is readily possible to obtain fairly developed spherulites from heated glycerol or ethyleneglycol solutions of PVA.

I would like to draw attention to the fact that the appropriate choice of a solvent may be essential not only for the character but for the possibility itself of the formation and development of ordered structures. This aspect of the problem is discussed in greater detail in the main lecture of Kang-Jen Liu[13]; however, we shall return to it when considering the so-called

specific ordered states resulting from specific polymer–solvent interactions. Here as two other examples of inherent diphility as a factor that can hinder crystallization, I could quote the behaviour of polymethacrylic acid in water and in methyl alcohol[14] or of tactic polymethylmethacrylate in the presence of precipitants having a preferential affinity either to the backbone or to the side ester groups, crystallization proceeding normally in the first case only[15].

Having thus answered the first question we still have not explained why on the right side of the coexistence diagram (*Figure 1*) one can obtain a practically stable solution. Take for instance, the state described by point A. The morphology of this state depends strongly on the way by which the point was attained. One possible way will be to start on the left side of the diagram (point B) and increase the concentration gradually by evaporation. Even in this simplest case the final condition will depend on the rate of evaporation. Obviously at least two events may happen: (a) The rate is sufficiently low: then nucleation may start, and in the unstable (towards the 'amorphous' phase equilibrium) region within binodals a gel will be formed with stable nuclei playing the part of the nodes of the gel framework. (b) When the rate is very high one can 'jump over' the amorphous instability range and attain the state A before both nucleation and spinodal phase decomposition have had time to start. This is a very primitive though illustrative example of a substantially 'thermokinetic behaviour' of the PVA solution: depending on the rate of increase of polymer concentration two distinctly different states can be attained, the second one being still thermodynamically unstable towards crystalline–amorphous phase separation, but *kinetically* stable toward this separation, and again thermodynamically stable toward amorphous phase separation.

In terms of the Flory–Mandelkern theory of the crystallization of polymers[7] we simply attain a state of supercooling where the nucleation rate becomes zero. However, this state exists, and it has its own partition function and free energy with corresponding configurational terms which differ drastically from those resulting in a low rate process.

In other words, if we ascribe to the initial state a free energy value F_B, the change of free energy, ΔF, *will not be* an unequivocal function of polymer concentration φ_2 depending strongly on the derivative $\partial \varphi_2 / \partial t$, t being time. Thus,

$$\Delta F = F_A - F_B = \int_0^t \left(\frac{\partial F}{\partial \varphi_2} \right) \frac{\partial \varphi_2}{\partial t} \, dt \qquad (1)$$

where $(\varphi_2)_{t=0}$ corresponds to the initial free energy, and $\varphi_2(t)$ though being the same in all cases, corresponds to *different* free energies and different stable or metastable morphologies. Hence the essential derivative in equation (1) is not $\partial F / \partial \varphi_2$ but $\partial \varphi_2 / \partial t$, all this being a primitive though correct demonstration of the thermokinetic approach. It should be pointed out that we deal with the usual thermodynamic quantities without applying the formalism of irreversible thermodynamics, but introducing explicitly some time derivatives. Equation 1 can also be presented in the form

$$\Delta F = \Delta F_0 \pm \delta(\Delta F) \qquad (2)$$

ΔF_0 being the 'equilibrium' value of free energy difference between states A and B corresponding to $\partial\varphi_2/\partial t \to 0$, and $\delta(\Delta F)$ being the above-mentioned 'correction term'. $\delta(\Delta F)$ can be of the same order of magnitude or even larger than ΔF_0.

The same state can be attained if one keeps φ_2 constant and lowers the temperature, T. Again, the form 2 of the change in free energy will hold, equation 1 being transformed into

$$\Delta F = \int_0^t \left(\frac{\partial F}{\partial T}\right) \frac{\partial T}{\partial t}\, \mathrm{d}t \tag{3}$$

which can be interpreted in an analogous manner. The essential point of all this discussion consists, however, not in the 'tricks' we do to avoid the usual description of relaxation phenomena accompanying supercooling, but in the reality of very different final morphologies of the system allowing different degrees of order (or disorder) that can be expressed in quantitative terms, for instance number of nuclei and degree of crystallinity.

3 'DEFORMATION OF THE BINODAL' AND RELATED CRITICAL PHENOMENA

In the lecture by Professor M. Gordon[16] very fine experiments are presented concerned with an abrupt interception of the binodal due to very rapid cooling. Though in Gordon's discussion the 'order' in the strict sense as noted in Section 1 is not formed, the process by itself is of great interest being closely connected with the possibility of different modes of nucleation.

The thermokinetic approach has an additional advantage allowing us to investigate the almost inverse situation, when due to an external field a point
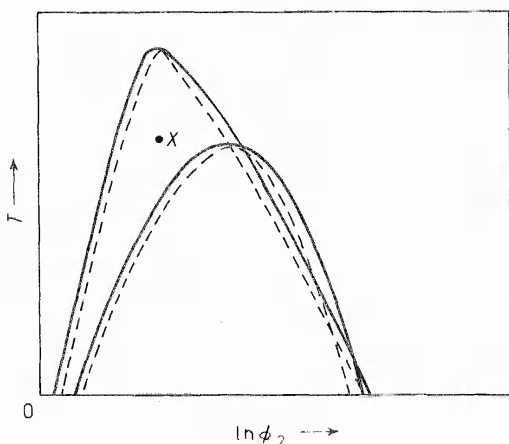

Figure 2. The deformation of the binodal. For details see text. The 'new' binodal is on the left

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(*Figure 2*) primarily situated in the one-phase region suddenly finds itself under the spinodal, φ_2 and the temperature being kept constant. In this case not only a pulse-induced critical scattering may occur but a spinodal phase separation can start in the same manner as described by van Aartsen and co-workers[17-19]. (The idea of the 'binodal deformation' was inspired by the excellent study by Pennings[20, 21] which led me to a reconsideration and new interpretation of some of my earlier work[22, 23].)

Imagine a case of a steady Couette flow with the concentration of polymer in the solution being sufficiently low and the viscosity of the solvent sufficiently high to produce some uncoiling due to the velocity gradient $\dot{\gamma}$. (It should be kept in mind that $\dot{\gamma}$ has the dimension s^{-1}, i.e. time^{-1}; hence again time dependent variables are introduced explicitly in the following considerations.) We suppose further that at a given value of $\dot{\gamma} = \dot{\gamma}_1$ the molecular coils do not overlap, the solution thus being 'dilute'. At a larger value of $\dot{\gamma} = \dot{\gamma}_2$ due to uncoiling the co-ordinational spheres of the macromolecules begin to overlap, and following the classical definitions of Debye and Flory[24] the solution can no longer be considered as dilute. The uncoiling and overlapping unavoidably bring relatively large portions of different chains into contact: hence due to the external field the configurational entropy of the solution as a whole is changed and consequently its free energy is also changed. One can postulate that the behaviour of the solution at a velocity gradient $\dot{\gamma}_2$ is equivalent to that of a solution at $\dot{\gamma} = \dot{\gamma}_1$ with an increased Flory–Huggins interaction parameter χ_1 (i.e. with a decreased solubility) and with increased rigidity of chains to account for the increase of coil dimensions. Later we shall see that this equivalence is not a formalistic mode of description but a fundamental physical fact. At any rate, and this is already an experimental fact, the gradient $\dot{\gamma}$ can attain a critical value at which the chains start to precipitate due to overlapping and contacting: in the case of crystallizable polymers a crystalline highly ordered precipitate forms. Just this is the main result obtained by Pennings for the case of stirring polyethylene solutions which were quite stable prior to stirring.

We return now to the phase diagram (*Figure 2*). If at $\dot{\gamma} = \dot{\gamma}_1$ the solution of concentration φ_2 is stable at a temperature T, and if $\dot{\gamma}_2$ is the critical value of $\dot{\gamma}$, then at the same concentration and temperature but at $\dot{\gamma} = \dot{\gamma}_2$ the solution becomes *unstable*. However, this means that now the state described by the same point $X(\varphi_2, T)$ is situated in the phase diagram *under* the binodal and, possibly, also under the spinodal. In other words, to account for the gradient-induced change in phase equilibria we must draw a new binodal shifted to the left and with a higher critical temperature. Just this transformation of the coexistence curve represents what I call 'the deformation of the binodal'. If one changes $\dot{\gamma}$ from $\dot{\gamma}_1$ to $\dot{\gamma}_2$ abruptly the state described by the point (φ_2, T) also abruptly 'falls' under the new binodal, so the overall process is truly equivalent to that described by M. Gordon.

Proceeding in this way Pennings recently succeeded in attaining crystalline-network films of polyethylene with tensile strengths up to 100 kilograms per square millimetre. However, even more pronounced effects of the same 'binodal deformation' kind are observed in the case of longitudinal flow: we shall discuss them in more detail in the section concerned with the stream–thread transition.

4 'ANTIPLASTIFICATION' AND SPECIFIC ORDERED STATES DUE TO SELECTIVE POLYMER–SOLVENT INTERACTIONS

4.1 The primitive kinetic approach; crystallization induced by plastification

The main aim of this sub-section is to remind one that in many instances the diluent plays a role of a 'kinetic stimulant' for crystallization. For example, it is very difficult to start nucleation approaching the crystallization temperature from the side of the glassy state, polyethyleneterephthalate being perhaps the only positively established case when such crystallization is possible. This possibility is due to the abnormally large difference between the melting and glass transition temperatures, T_m and T_g. If in the case of any other polymer by addition of a diluent one can decrease T_g more than T_m, a situation is frequently attained which is favourable towards crystallization. There exists a well known practical rule: to induce crystallization in a polymer that does not crystallize due to kinetic hindrances, one must add a diluent which is a poor solvent for this polymer[7]. Being a poor solvent (the interaction parameter χ_1 is large) such a diluent practically does not affect T_m but lowers sufficiently T_g thus providing the amount of mobility of the chains necessary for nucleation.

From the point of view of molecular physics the situation with such polymers is just the same as in the case of kinetically stable solutions of PVA: thus we can call otherwise crystallizable polymers that fail to crystallize solely for kinetic reasons, 'kinetically stable' in the amorphous state. One such polymer is probably poly(vinyl chloride) (PVC), and a lot of papers dealing with its 'antiplastification'[25] demonstrate, in my opinion, the formation of stable nuclei that cannot, however, grow further, due, again, to the inherent diphility of this polymer and their being either less ordered or smaller than the corresponding nuclei in PVA. Hence, in this case the 'antiplastification' is (probably) the result of the kinetic stimulation of nucleation.

4.2 'Real' antiplastification: ordered structures that can be formed only in the presence of solvent or diluent

There exists, however, another class of ordered polymer–solvent systems where the order itself exists only in bicomponent systems. Probably the first data of this kind (though not quite typical: the effect is 'damaged' by an 'admixture' of the primitive effect described in the preceding subsection) are found in a relatively early paper of Kargin et al.[26]. They observed the formation and disappearance of isotactic polyacrylic acid spherulites on alternating dilution and evaporation or heating and cooling. The essential fact in their study was that the spherulites of the same size and shape appeared in the same places, as registered by polarizing microscope photographs.

Also in early work with Shaltyko and Agranova[27] I observed very similar behaviour in poly-γ-benzyl-L-glutamate (PBG)–solvent systems. There was, however, an essential difference in this case from the preceding one, namely, the spherulites were disappearing at polymer contents approximately 85 to 90 per cent (w/v), and reappearing at the same places—and in general being *the same ones*—on isothermal dilution with dioxane which is known as a helix-promoting solvent for PBG.

On a later reconsideration of this work we proceeded in the same manner using as a solvent the dichloroacetic acid (DCA) which is well known as a promotor of the helix–coil transition in PBG. However, in this case we
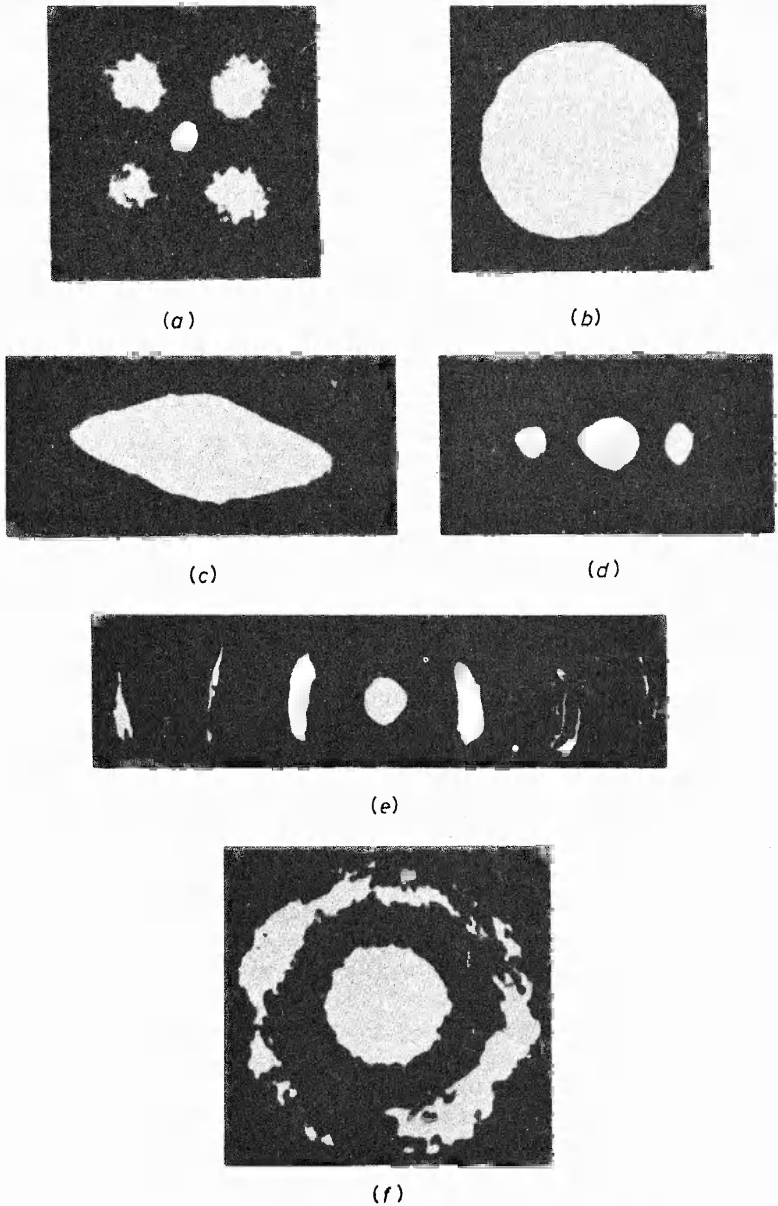

(a)

(b)

(c)

(d)

(e)

(f)

Figure 3. The development of liquid crystalline morphoses in the system PBG–DCA after the isothermal coil–α-helix transition[28] a—liquid spherulites; b—the collapse of 'diluted' spherulites; c—the appearance of the nematic phase; d—the scattering from the cholesteric phase; e—the formation of the 'phase-amplitude diffraction grating' in the solution; f—the scattering after some stirring of the solution in state 'e'. In all cases H_v-scattering

observed very different events at different concentration ranges. At a low concentration, just as one should expect, the solution was isotropic, and the PBG molecules existed in the random coil conformation as revealed by i.r. spectroscopy measurements. In the intermediate concentration range (the crucial concentration being dependent on molecular weight and temperature) an isothermal transition coil–α-helix takes place (checked by the amide I band), after which a whole set of liquid crystalline morphoses develops gradually (*Figure 3*, polarized small angle light scattering data, H_v-patterns). It should be mentioned that some similar morphoses but not as abundant were observed earlier by Robinson[29] who used polarizing microscopy only. At yet higher concentrations of PBG the situation with dioxane is repeated: in the 75 to 85 per cent PBG range liquid (?) spherulites appear. differing in shape, size and amount of order from those formed immediately after the coil–helix transition, but as DCA evaporates (without heating!) the spherulites collapse. If a drop of DCA or dioxane is inserted on the film with collapsed spherulites they reappear in the same place.

Though this study was described in detail in several papers[28, 30, 31], I should like to call to mind one specific feature of the most ordered morphose (*Figure 3e*) which was interpreted as optically equivalent to a phase-amplitude diffraction grating (the similarity of this polarized light diffraction pattern to wide angle x-ray diffraction patterns of highly oriented polymers also deserves some attention). This morphose displays two distinct temperature induced order–disorder transitions, each of them being a specific orientational melting, following J. Frenkel's[1] terminology (*Figure 4*). First to disappear is the higher range of order (cholesteric) as measured by the intensity of the first order reflection. However, in the course of a decrease of intensity the spacings
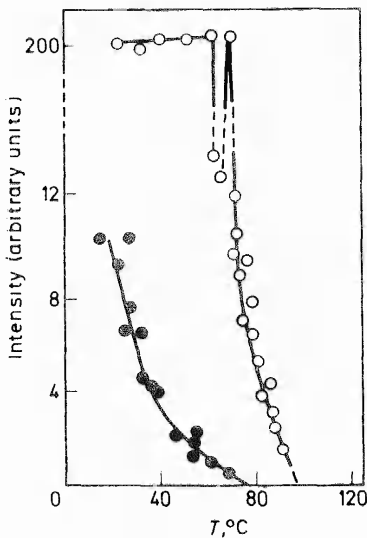

Figure 4. Orientational melting in the system PBG–DCA with the high degree of order (state 'e' of *Figure 3*). Black circles—1st reflection; open circles—the central spot

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also decrease gradually, as if a desolvation of DCA proceeds[30] leading to an improvement of the liquid crystalline frame (quite an opposite behaviour was observed with dioxane as solvent[32]). With decreasing intensity of the first reflection the intensity of the central spot increases and splashes abruptly at the temperature of the first transition (71.5°C). Hence, the scattering intensity of the higher range of order is 'pumped over' into that of the lower one, which is probably simply nematic. This order persists, on further heating, until at 95°C a second orientational melting takes place, and the solution becomes isotropic, the macromolecules pertaining to the α-helical conformation as i.r. data indicate.

Thus a somewhat contradictory behaviour is displayed by PBG in different concentration ranges, DCA acting as a 'real' antiplastifier in the high concentration range only. However, an element of contradiction appears also within the liquid crystalline range, the higher type of order simultaneously improving (as the decrease in the 'interplanar distances' show) and gradually melting. Probably this observation together with the above-mentioned 'pumping over' is of general importance showing the possibility of temperature induced transitions proceeding in opposite directions (in respect to order) on different levels of structural (the Russian adopted term is 'supermolecular'[33]) organization. Moreover these data are a non-direct evidence of the coexistence of *two* (or more) liquid crystalline phases, as predicted by Flory's general treatment (see for details Miller's lecture[42]).

Returning to the isothermal concentration induced coil–helix transition followed by a phase transition from an isotropic solution to the liquid crystalline state, one must interpret it according to the Flory–DiMarzio[34, 35] theory of formation of a nematic phase by semiflexible chains. However, a simple interpretation in terms of a constant flexibility parameter f (being the molar fraction of 'flexible' bonds in the chain) and the corresponding critical concentration is here impossible. Again, though discussed elsewhere, it should be remembered that the same PBG sample ($M_w \approx 10^5$ with a narrow molecular-weight distribution) displays in dioxane quite another behaviour, starting to form liquid crystalline morphoses even at 7 to 8 per cent. At this same concentration, however, in DCA the macromolecules are still statistical coils with a supercritical value of f (i.e. $f > 0.63$) and thus incapable of forming a nematic phase at any concentration. What makes the phase transition possible is an abrupt change of the conformation of PBA leading to a change of the f value near to zero.

As was first pointed in our work with Elyashevich[36] and further discussed in my short communication at this Symposium[37] this means that the change of χ_1 at a specific PBG concentration φ_2^1 (and correspondingly DCA concentration $\varphi_1^1 = 1 - \varphi_2^1$) is such that the exponent $(\Delta\chi_1/kT)\varphi_1^1$ in the formula for the resulting flexibility coefficient

$$ f = f_0 \exp\left(-\frac{\Delta\chi_1}{kT}\varphi_1^1\right) \Big/ \left\{ 1 - f_0 + f_0 \exp\left(-\frac{\Delta\chi_1}{kT}\varphi_1^1\right) \right\} \tag{4} $$

is close to infinity thus turning f to zero, f_0 being the initial supercritical value of f. Such a catastrophic change (I was tempted to give this set of events the name of 'conformational catastrophe') may be due only to a desolvation— just of the same kind as described by Doty[38] for dilute PBG solution in

DCA–dichloroethane mixtures on heating (in a certain composition range).

The peculiar behaviour of PBG in a higher concentration range is probably connected with thermokinetic rather than thermodynamic reasons, the rodlike helical macromolecules being incapable of rearranging themselves in a crystalline array without the aid of some external field that will induce a new α–β conformational transition. Thus it is possible that the addition of DCA to a dried film on a supporting glass plate stimulates a series of local α–β transitions, the necessary energy being provided by surface tension, and the β-conformation being more suitable for packing of the chains into three-dimensional crystalline units which in their turn are packed in a spherulite or a similar morphose. In this respect (the energy is provided by surface tension) the reaction of the film on dioxane is interpreted similarly.

It should be pointed that this last interpretation is still hypothetical. contrary to that concerning the real liquid crystalline state of PBG. However. DCA in different concentration ranges produces undoubted intramolecular disorder–order transitions which are followed by transitions of related kind on higher structural levels. The source of all these effects is the specific and concentration dependent PBG–DCA interaction. most probably of a 'solvation–desolvation' kind. thus supporting the ideas presented in the lecture of Dr Kang-Jen Liu[13].

Quite recently a very similar behaviour of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) spherulites was reported by Horikiri and Kodera[39]. These authors were able to show directly that after the collapse of spherulites due to solvent elimination the dried and solvent free films were amorphous as checked by different methods. The addition of solvent led to an intense spherulitization showing just as in the preceding case that the presence of solvent (in the strict sense of the word—not 'diluent' or 'plastifier') is necessary not only to stimulate crystallization, but—which is far more important—*to stabilize the crystalline phase.*

Though the term 'antiplastification' arises from technological slang, if we still adopt it and want to ascribe it some physical meaning, we must denote by antiplastification a specific mechanism of stabilization of the crystalline (or other ordered) state in the presence of solvent.

This brings us back to another study made by us in the sixties[40] where real x-ray detected crystallization was possible only in the presence of solvents. each solvent (formic or acetic acid, or phenol) producing a somewhat different unit cell. The polymer was poly(octamethylenedibenzimidazole) (POMBI) with the repeating unit
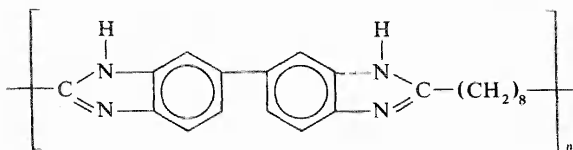
In this case it is probably possible to obtain the f-value by direct calculation : however, it is beyond doubt that on shortening of the methylene sequence f will decrease. The tetra-analogue of POMBI gave a rich x-ray pattern : there were some difficulties in obtaining the hexa-analogue in the crystalline

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state (in this case the action of formic acid being a mixture of kinetic stimulation and 'real antiplastification'), and with POMBI it was quite impossible to obtain a dry crystalline film or fibre, though in the latter case one could observe some traces of a not very developed unidimensional order.

Hence, simple logic leads to a conclusion that the increased flexibility of oligomethylene links between the bulky dibenzimidazole groups makes an ordered packing impossible. Again we must turn to equation 4 and suggest that some specific interaction of the solvent (usually, formic acid), with the polymer will this time be a kind of solvation (thus, a 'positive' interaction, as compared with PBG–DCA system in the intermediate concentration range). The solvated POMBI chain at some polymer:solvent ratios behaves as a complex with increased rigidity making it similar in respect of crystallizability to the $(CH_2)_4$-analogue. To account for this change of flexibility one must calculate the changes of free energy for the amorphous and crystalline states of the polymer–solvent system. The calculation leads for the free energy in the crystalline state

$$\Delta F_{cr} = \chi_c \varphi_1 + (C\varphi_2 - \varphi_1) \ln \frac{C\varphi_2 - \varphi_1}{C\varphi_2} + \varphi_1 \ln \frac{\varphi_1}{C\varphi_2} + \Delta F^0_{\varphi_1 = 0} \qquad (5)$$

Here χ_c is the Flory–Huggins parameter in the bicomponent crystalline lattice, C is the stoichiometric number of solvent molecules that can be bound with one chain repeating unit, and $\Delta F^0_{\varphi_1 = 0}$ is the free energy of the polymer with the same lattice in absence of the solvent. Equation 5 holds for
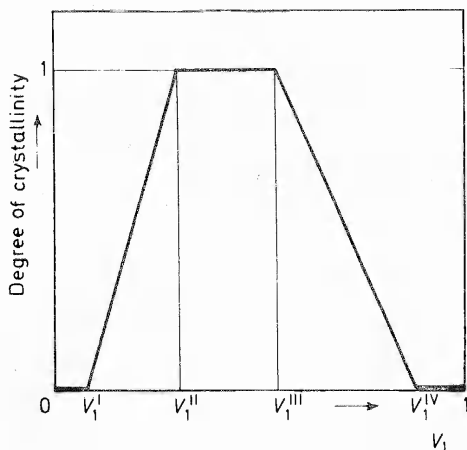

Figure 5. The coexistence diagram of crystal-solvates[36]. The volume fraction of the solvent is plotted on the abscissa (φ_1 in the notation of this paper)

$\varphi_1 < C\varphi_2$. At $\varphi_1 = C\varphi_2$ the lattice is completed, and this concentration corresponds to the minimum of free energy for the crystalline state, though crystallization starts actually at lower solvent concentrations. At $\varphi_1 > C\varphi_2$ the solvent can no longer enter the lattice without damaging it. Figure 5 illustrates the situation. It can be seen, again, that the crystalline state is

wholly stable only in an intermediate range of polymer:solvent ratios. dissolving on dilution and gradually 'melting' at concentrations $\varphi_2 \geqslant 1 - \varphi_1^{\Pi}$.

As to the mechanical properties of POMBI fibres, in the crystalline state they are sufficiently poor. However, after thermal treatment, elimination of solvent and loss of three-dimensional order the tensile strength improves essentially attaining values as high as $70 \, \text{kg mm}^{-2}$. Hence, one should conclude that the crystals observed are plastic in nature. The same is most probably the case for PBG at low DCA concentrations and for the collapsing PPO spherulites. It follows that the choice between notions 'plastification' or 'antiplastification' is in this case a linguistic rather than physical problem.

## 5 THE NATURE AND SOME DYNAMIC PROPERTIES OF POLYMERIC LIQUID CRYSTALS

Much attention has been devoted to liquid crystals in this Symposium, both in the main lectures and in short communications. Two distinctly different types of ordered mesophases were discussed : one, containing rod-like or at least sufficiently rigid chains (with subcritical values of Flory's parameter: $f \leqslant 0.63$), and the other formed by block-copolymers. We shall discuss very briefly both kinds paying more attention to their common properties than to differences.

5.1 Tactoid and related systems

These systems obey in general the laws following from the theories of Flory and DiMarzio[34, 35]. However, as can be seen from the data already presented, it is not necessary to treat their nature as essentially entropic[42]. and purely energetic factors, such as specific polymer–solvent interactions or external influences on the chain conformation (see below) should be taken into account.

In this subsection I shall try to apply some of the recent criteria developed for ordinary liquid crystals to the polymeric ones, and in particular to the problem of their domain structures, the boundaries between domains being formed by disinclinations.

As an example of a 'classical' Flory–DiMarzio polymeric liquid crystal. the poly(p-benz)amide (PBA) has been chosen. which was studied in detail by Papkov and co-workers in the USSR[43–45]. Statistical mechanical considerations in Flory's[46] manner lead to a conclusion that in the case of *trans*-configuration of the amide bond the PBA chain

$$\left[-N -\!\!\!\bigcirc\!\!\!- \underset{\underset{O}{\parallel}}{C} - \right]_n$$
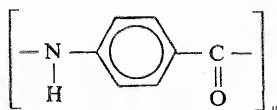
must be fairly rigid ($f \to 0$) in spite of the possibility of the rotation of the benzene ring. The behaviour PBA displays in dimethylacetamide with 3 per cent lithium chloride added is characteristic of rodlike macromolecules both in the high and medium dilution range. For instance, the critical concentration of the formation of the tactoid phase

$$\varphi_2^* = \frac{8}{p}(1 - 2/p) \qquad (6)$$

is distinctly observed, the axial ratio p being of course pro oo tional to the molecular weight; further, the intrinsic viscosity is connected with p or M_w by an exponential formula of the usual type $[\eta] = K_\eta M_w^a$ but with a value of a close to 1.7, which, according to Simha, is the limiting value of the exponent for rodlike particles[47].

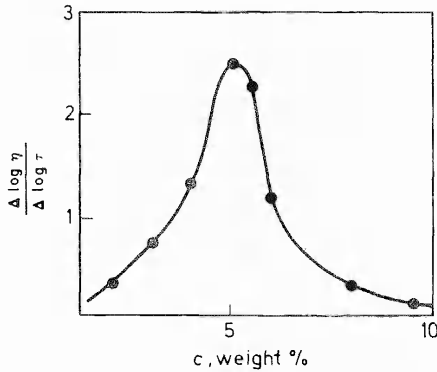However, most striking are the absolute viscosity data. *Figure 6* shows the

Figure 6. The concentration dependence of the 'viscosity anomaly' of PBA

viscosity shear stress relation as a function of the concentration of PBA. and *Figure 7* shows the zero shear viscosity of the same sample as a function of temperature. We shall omit different rheological data concerning the
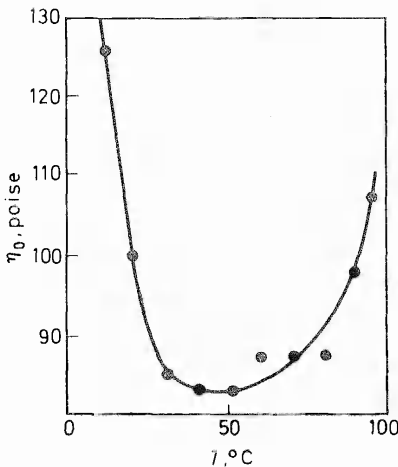

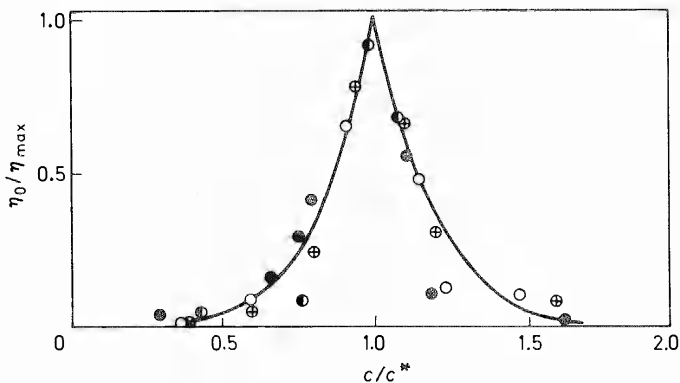*Figure 7.* The temperature dependence of the viscosity of a 5.5 per cent solution of PBA

Figure 8. The dependence of the reduced absolute viscosity on the reduced concentration of PBA
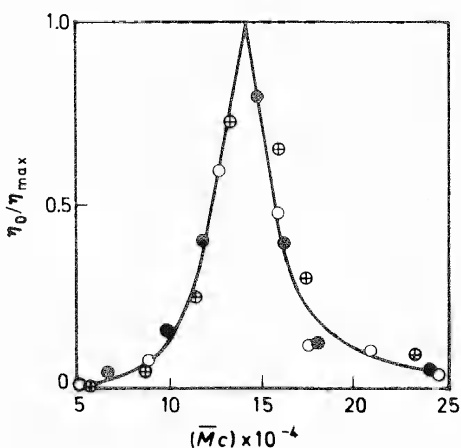

Figure 9. The reduced absolute viscosity of PBA as a function of the product $\overline{M}c$

master curves and related forms of representation, but some intermediate plots should be mentioned (*Figures 8* to *10*). There are distinct singularities in the dependences of reduced absolute viscosities on reduced concentrations or on the product $\overline{M}c$, the critical value of the latter being in all cases 1.3×10^5 at $20°C$ (c expressed in weight per cent).

All those singularities indicate that at a given molecular weight and concentration the PBA solution undergoes a phase transition from the isotropic to anisotropic state, the critical values on the abscissae allowing us
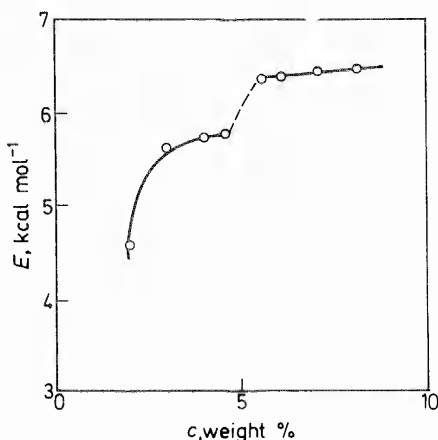
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Figure 10. The concentration dependence of the energy of activation of viscous flow of PBA

to check the position of the binodal (*Figure 11* : the investigated temperature range is shown). Finally, x-ray data show a gradual decrease of interplanar distances with PBA concentration, these distances becoming constant after a specific (for the given sample) concentration is attained.
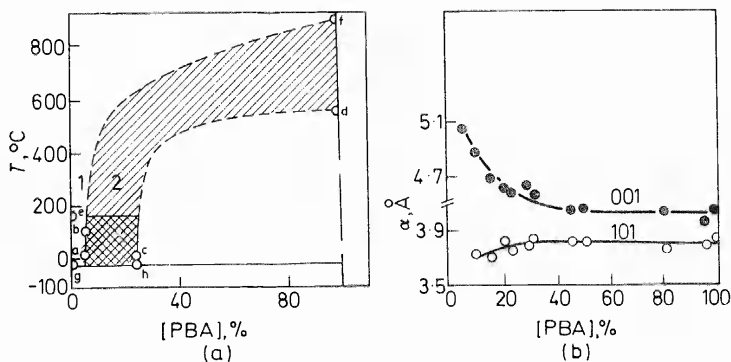

Figure 11. a—A part of the phase diagram of PBA. The hatched region (2) corresponds to the liquid crystalline state: the region actually evaluated is marked by cross-hatching. b—The concentration dependence of interplanar distances in PBA. The reflections are noted above the corresponding curves

The abrupt fall of the viscosity after the intersection of the binodal can be explained in one manner only : the mechanism of flow itself undergoes a change, the real viscous flow (with all anomalies peculiar to polymers) being changed into a slip along the disclinations or the domain boundaries.

One rather important observation, this time of a technological nature, should be added. Turning to the American data[48, 49] obtained with the

same polymer or with poly(phenyleneterephthal)amide, very similar both in structure and properties, or, with a 100 per cent *para*-aromatic polyamido-hydrazide which displays a very similar behaviour (these polymers being connected with the so called 'Fiber B' and 'Fiber X'), one can draw the conclusion that on wet spinning the solutions of these polymers allow the attainment of very high modulus and tensile strength in these cases only when one proceeds with spinning from the *anisotropic* state. The overall draw ratio in this case, as a rule, does not exceed 150 per cent. The most probable explanation of these results is that some sort of 'stocks' of the future fibre preexist in the solution, these stocks being the unperturbed domains. The mechanical longitudinal field during spinning packs the domains one along another in such a manner that the internal orientation in the domains coincides with the overall orientation. This statement is equivalent to the suggestion that the domains disappear, the whole sample attaining the state of a 'liquid single crystal'. That it really can be a case is shown by the data on the behaviour of the PBA solution in a strong magnetic field which I presented in one of the short communications at this Symposium[37] (see also *Figure 12*). In this case again the external field
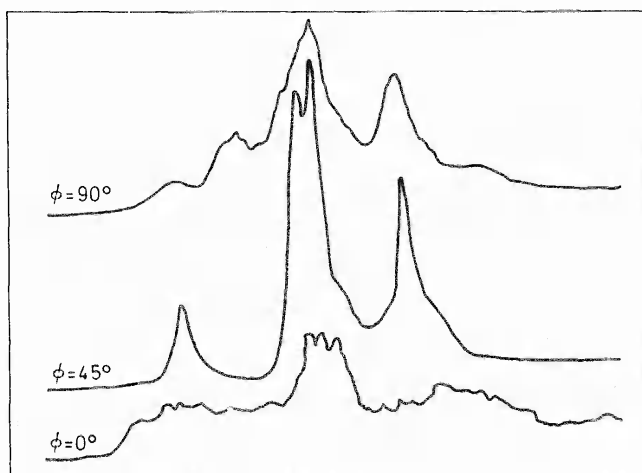

Figure 12. The anisotropy of p.m.r. spectra of dimethylacetamide at PBA concentrations higher than 8 per cent (by weight). ϕ—the angle between the orientation of the solution (attained before the rotation of the cell and persisting a short time after the turn) and the new orientation of the magnetic field (in the co-ordinate system of the sample)

reorganizes the overall structure on its highest (on the scale of dimensions) level promoting a very specific spatial uniaxial orientation, the solvent molecules participating in the organized macromolecular frame. If one changes the direction of the magnetic field or turns at the same angle the cell with the solution the latter reorients as a whole following the new field direction, the time of structural relaxation (or rather retardation) being approximately 30 minutes. Here also critical parameters exist, one of them

being the concentration (or product $\bar{M}\varphi_2$), and the other the field intensity that must be of the order of 10^4 Oersted units. At lower fields no such effects are observable. The field-induced spatial nematic order is retained to some extent after switching the field off, the relaxation time (of reestablishment of the initial domain structure) attaining several days or even a week.

An effect similar in nature was previously observed by the Japanese for PBG[50].

However, in our case the structure and mechanical behaviour of a PBA film obtained in these conditions were estimated. The film has a practically zero tensile strength in the direction normal to that of the force lines of the magnetic field, fibrillating spontaneously along these lines. This is just the behaviour one should expect from a flat nematic solid single crystal. For further discussion, the analogy of this fibrillization in the rigid-chain, wholly-oriented system with that occurring in superoriented flexible chain polymer films should be kept in mind.

5.2 The mesophases in binary and sandwiched block copolymers

Turning to this type of liquid crystal one can immediately see a striking difference in morphology as demonstrated in the main lecture of Dr B. Gallot[51]. All periodic structures presented belong to higher levels of organization, the lower level being formed by an assembly of crystallizable (or noncrystallizable!) blocks and having an *ordinary* crystalline (or amorphous) structure. These primary units are assembled in their turn in one or other type of supermolecular organization characterized by x-ray large periods. This is the case where higher order structons appear quite definitely. One can mention at least two levels of packing. The first is formed by segregated blocks, whose aggregation leads to fairly monodisperse superunits, not necessarily crystalline. However, the mere fact that their dimensions are equal (due, of course, to the extremely narrow distribution of block length) makes possible their further packing in a fully ordered array which has every 'right' to be called crystalline, as has any fixed geometrically-ordered spatial distribution of equivalent units.

The diphility and resulting specific block–solvent and block–block interactions play in this case the role of a 'driving force' of a purely thermodynamic nature, which 'triggers' and further promotes the whole ordering process. It is a possibility (though needing more direct confirmation) that in the case of cylinders they behave as Flory's tactoids following the general scheme of formation of a tactoid (nematic) phase. This possibility is to some extent substantiated by the fact that under specific flow conditions (i.e. when the system is subjected to the action of an external field) the ordering may proceed at elevated temperatures *in the absence* of solvent, as was shown in the very fine study of the Bristol group (A. Keller *et al.*, short communication presented at this Symposium). Thus, the thermodynamic driving force may be substituted by a mechanical one, leading to the conclusion (which is preliminary, still needing more direct support) that the systems under consideration enter into the frame of the equivalence principle discussed below (Section 6). There are several other features common to the systems ordered by segregation phenomena and to those formed by rigid macromolecules.

(*i*) As a rule, the macromolecules able to form liquid crystalline meso-

phases are diphilic—either inherently or in the explicit form. All block copolymers present an extreme case of diphility, each block having its 'own' preferential or selective solvent which usually behaves differently towards the other type of blocks. As is well known, in dilute solution this diphility results in the formation of molecular micelles[52, 53] which are visualized as insoluble 'nuclei' still kept in solution by the soluble block or blocks. Without doubt, if the insoluble block is crystallizable and flexible it will form a folded crystal nucleus, the nucleation being monomolecular. Thus the growth of lamellar crystals from blocks of only one kind is inevitable due to secondary nucleation proceeding in the same manner when the overall concentration is increased. The lamellae are still held in solution or gel, by the soluble blocks, thus forming one of the special cases of liquid crystals. The styrene–ethylene-oxide block copolymers are an example.

If we return to PBG the very same type of behaviour is observed if the affinity of the solvent for the side groups is sufficiently greater than for the polypeptide backbone. The solubility of helical PBG as compared to the *in*solubility, for instance, of helical poly-L-alanine may be explained in the same terms as the formation of molecular micelles. The α-helical backbone is *essentially desolvated*, forming some kind of intramolecular 'linear-crystalline' structure (about the classification of intramolecular structures see Ref. 54) which one can visualize as an insoluble spring still held in solution by the side groups. This model accounts fairly well for the desolvation effects discussed in the preceding section.

The behaviour of PBA could be explained in a similar manner, though the discussion of the details would lead us far aside from the main item.

(*ii*) The diphility and the connected segregation effects, especially in the presence of selective solvents, may give rise to crystallization or liquid crystallization mechanisms of the same type as discussed above (variation of solvent leading to sufficiently strong variation of χ_{1A}, the second subscript indicating the crystallizable block in the case of block copolymers). It should also be kept in mind that the non-crystallizable block in the case of partial compatibility may affect the glass temperature of the crystallizable block, thus providing better kinetic conditions for crystallization.

(*iii*) In the case of *in*compatibility of two blocks both being soluble in a common solvent at least one of them may attain, as a result of segregation, a subcritical f value which is followed as concentration is increased by formation of nematic or cholesteric domains.

One could proceed with (*iv*), (*v*) ... etc.: however, any attempt at a further, even qualitative analysis will be premature, for the preceding discussion was held mainly on a hypothetical, though not improbable, basis. Nevertheless, the concept of diphility and resulting 'partial solubility' as necessary conditions for the formation of liquid crystals or other specific bi- and tri-component ordered states in which the solvent participates *actively* is not a hypothesis and may turn out to be the 'common denominator' for all known types of polymeric liquid crystals. If this is true, then Flory's formalism in the modification with the variable flexibility parameter and incorporation of higher order structons (tactoids formed by aggregated blocks) will also hold for all cases of ordered structure formation. In the next section we shall try to show that the same is true in the presence of external fields.

6 NUCLEATION AND CRYSTAL GROWTH IN THE PRESENCE OF EXTERNAL FIELDS AND THE EQUIVALENCE PRINCIPLE OF THERMOKINETICS

Now we return to the thermokinetic treatment of the formation of ordered structures in dynamic conditions. One should immediately note that Zachmann's treatment[55] is wholly applicable to these conditions when the external field drastically affects both the long range diffusion of chain segments and the probability of incorporation of a new chain in the growing crystal. However, this is a problem of orientational crystallization that will be treated in the end: just now we shall consider the direct application of the equivalence principle to systems subjected to longitudinal flow.

6.1 Stream–thread transition and the 'orientational catastrophe'

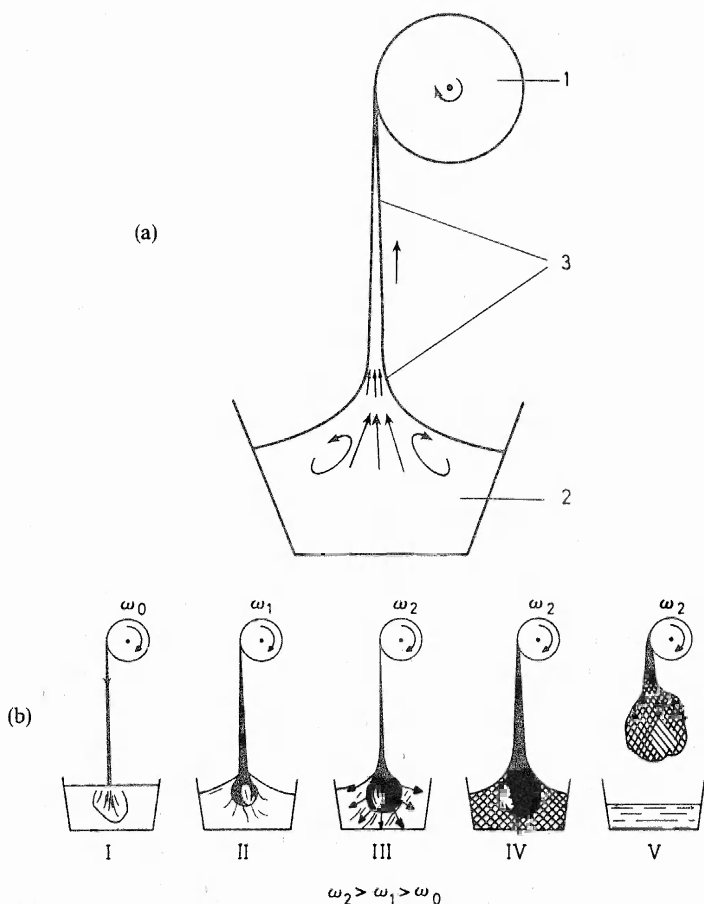Our earlier work[22,23] that was reconsidered recently consisted in

Figure 13. a—Schematic representation of the method of generating a stationary jet. 1—Rotating cylinder; 2—solution; 3—region of stable longitudinal flow. b—Orientational catastrophe with the fibroin solution. The arrows show the direction of propagation of the perturbation wave

generating a stable liquid filament by means of a rotating cylinder (*Figure 13*) the height of which above the level of the polymer solution and the angular velocity ω could be varied. The solutions studied were PMMA in dimethylformamide and silk fibroin *Bombyx mori* in acetone–lithium bromide solution with some admixture of water. Only visual observations of the stream–thread transition were made, some of them substantiated later by means of polarized light scattering with a laser as a light source.

As was described in 1965, the transformation in PMMA at increasing ω starts with the appearance of strong birefringence followed by opacity. The stream ejects macroscopic drops of the solvent (probably not pure solvent; see below), and at very high ω or, which is the same, longitudinal velocity gradients $\dot{\gamma}$, a kind of fog is observed around the stream.

The fibres thus formed still contain approximately 30 per cent of solvent and are strongly birefringent. Being kept in a free state they gradually lose the solvent and contract, the birefringence disappearing and thus showing the relaxation of chain orientation. However, under isometric conditions, when the fibre cannot contract, an internal stress of the order of 25 to 50 kg mm^{-2} develops, and at some ultimate moment depending on the remaining solvent concentration the fibre 'annihilates' being not merely torn but 'exploded' into powder by internal stress. This first kind of orientational catastrophe strongly resembles the well known 'annihilation' of inorganic glasses on spontaneous crystallization.

The second type of orientational catastrophe observed with fibroin is even more spectacular. In this case one can follow the propagation of the crystallization (or, rather, solidification wave) in a direction opposite to the direction of flow, the solution changing in colour from light yellowish-brown to dark brown. This wave (*Figure 13*) attains the level of the liquid and then expands in the bulk of the solution, which is finally pulled out of the
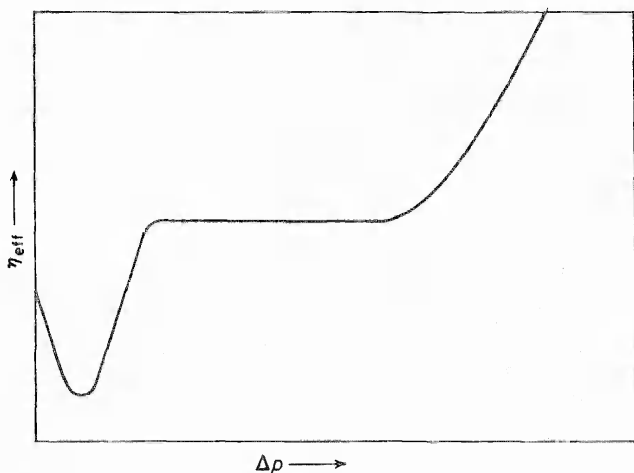

Figure 14. The dependence of the effective viscosity on the longitudinal velocity gradient. (In the actual conditions of the experiment[22] the pressure decrement Δp was measured in the jet viscometer instead of $\dot{\gamma}$: Δp is proportional to $\dot{\gamma}$)

vessel as a gelated bulb. An estimate of the tensile strength of the filament needed for this process gives again a figure of approximately 50 kg mm^{-2}.

Knowing the structure of fibroin and the ability of its crystallizable peptides to display the $\alpha \to \beta$ transformation, one can explain this catastrophic transition in the stretched solution by just such a transformation induced by stretch. *Figure 14*, showing the so called complex flow of fibroin solutions, substantiates this conclusion. The minimum of effective viscosity η_{eff} occurs as a result of competition between ordinary (shear) and longitudinal flow[23]. After the minimum is attained the latter predominates, a positive feedback being established between longitudinal viscosity $\bar{\bar{\eta}}$ and the rate of strain. The first increase of η_{eff} is due to uncoiling, and the plateau region corresponds to a kind of steady state where sufficient energy must be accumulated to produce the $\alpha \to$ coil $\to \beta$ transformation of the molecular level. The second rise of $\bar{\bar{\eta}}$ (the shear viscosity being now negligible) is due to the abrupt increase of multilateral interaction of the extended chains. this interaction proceeding as a formation of interchain hydrogen bonds characteristic of the β-conformation of polypeptides.

To explain at least qualitatively the phenomena described one must accentuate their main features. There are:

(i) The strong birefringence of solvent containing PMMA fibres and their collapse on loss of solvent;

(ii) The occurrence of a crystallization or perturbation wave moving in the direction opposite to that of flow;

(iii) The ejection of solvent at increasing angular velocities during the transformation.

Features (i) and (iii) resemble the collapse of PBG or PPO spherulites on isothermal evaporation of the solvent, and the desolvation phenomena in the PBG–DCA system leading to formation of liquid crystals, respectively. Feature (ii) needs deeper consideration. The initial state and the state preceding the expansion of the perturbation wave in the volume of fibroin solution present just the case discussed in a general manner in Section 3 (*Figure 2*). The orientational catastrophe with the fibroin solution being transformed to a cross-linked gel is a *very typical spinodal phase separation* resulting from the 'deformation of the binodal'. The stress induced conformational change leads to an immediate increase of the Flory–Huggins parameter χ_1, strong desolvation of chains and substitution of polymer–solvent contacts by polymer–polymer hydrogen bonds.

It should be remembered further that according to Cahn's theory of spinodal phase decomposition verified for polymers by van Aartsen and co-workers[17–19], there are some preferential directions of growth of the composition fluctuations. As pointed out by Cahn[56], in the case of metal alloys or glasses these are some lattice directions. In van Aartsen's studies there were no such directions, but in our case such a direction again appears. and it is, of course, the direction of stretch. Thus, the perturbation wave observed represents the front of fluctuations expanding along this preferential direction.

If we turn to the F–T formalism, then the situation is presented as follows (*Figure 15*). The stable solution of the crystallizable polymer (fibroin) may exist at a given concentration in two states—crystalline and amorphous.
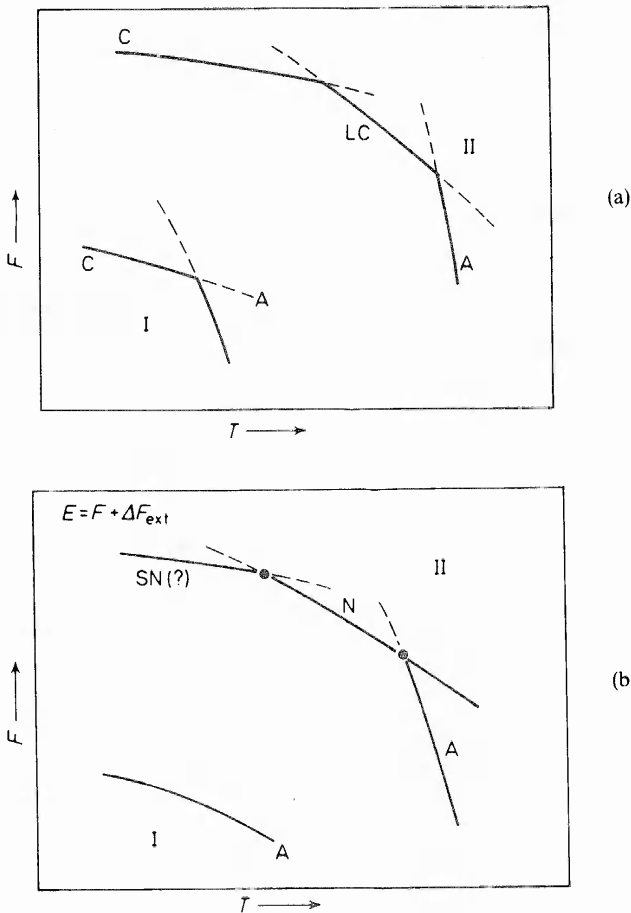
Figure 15. The illustration of the stream–thread transition on the F–T diagram. I—unperturbed system. II—a stretched system. a—fibroin. b—PMMA. Notations of states: A—amorphous; C—crystalline; LC—liquid crystalline (any kind); N—nematic, SN—solid nematic. The interrogation sign denotes the doubtfulness of its stability : see text

with a transition point (*Figure 15a*). A hypothetical full analogue of fibroin differing from the latter only by the value of the flexibility parameter, f being subcritical, will display a different behaviour (the upper set of curves on *Figure 15a*), existing in three possible states—crystalline, nematic, and isotropic. However, by subjecting the solution to the action of a mechanical field we *in fact changed* the initial value of the flexibility parameter f_0 to a new one

$$f = f_0 \exp\left(-\Delta\varepsilon/kT\right)/\{1 - f_0 + f_0 \exp\left(-\Delta\varepsilon/kT\right)\} \tag{7}$$

$\Delta\varepsilon$ being the part of the external field energy ΔF 'pumped over' in the internal energy of the chain limiting its freedom of rotation, the other part of this

energy affecting the configurational entropy of the solution with chains already extended.

Hence, from the point of view of Flory–DiMarzio theory there is *in fact* no difference between the behaviour of an unloaded solution of inflexible molecules and a loaded one of flexible molecules. The equivalence comprises not only the kinetics and morphology of phase separation, but also its thermodynamics, for desolvation *in fact* occurs and the additional energetic term $\Delta\varepsilon$ can be substituted by $\Delta\chi_1\varphi_1$ from equation 4.

However, this equivalence may also be treated as just a special consequence of another general principle advanced by Katchalsky and Kuhn—the teinochemical principle[57,58].

The situation with PMMA is very similar in its general features (*Figure 15b*); however, due to the fact that it cannot form an organized phase at rest only one state is possible in the untreated solution. But when this solution is stretched, again, a spinodal phase separation occurs, the more dilute phase being ejected from the stream and the more concentrated rearranging itself into a nematic phase. Just at this point an essential difference between fibroin and PMMA should be noted. In fibroin the ordered state, either nematic or crystalline, is fixed due to hydrogen bonding. In PMMA the ordered state can be sustained only on the condition that some external force equilibrates the rubber-like internal entropic stress which leads in the free state to contraction. In addition, the nematic state needs some amount of solvent for its stabilization, the elimination of solvent leading to multiple fracture ('explosion'). Of course, the cause of the orientational catastrophe with PMMA is the high amount of (mechanical) energy absorbed by the system and not released as heat of crystallization.

Discussing the stream–thread transition in thermokinetic terms and using the equivalence principle one must not forget about the purely mechanical side of events and the existence of the Poisson coefficient adding a 'mechanical term' to the desolvation energy $\Delta\chi_1\varphi_1$. In addition, in the course of desolvation (or solvent ejection, which is the same at first approximation), both $\Delta\chi_1$ and φ_1 change in different directions, but this does not affect the general qualitative physical treatment presented.

At the end of this subsection I would like to make two remarks not directly connected with the main item but following from the binodal deformation and corresponding F–T formalism.

(i) Many unsuccessful attempts to obtain fibres from globular proteins are due to the fact that their diphility towards moisture is ignored. One can proceed with ordinary spinning using ordinary processing for these proteins, but their behaviour will be the same as for PMMA filaments though for other reasons. The so-called Fisher diagram[59] (*Figure 16*) shows a general correlation between the linear dimensions of proteins in water and their hydrophobic amino acid content. All natural protein fibres are formed by proteins situated in the upper left side of the diagram, the globular proteins being spread along the right side of the regression curve. The parameter L on Fisher's diagram formally corresponds to a χ_1-dependent value of the flexibility parameter. One *can* extend the chains of the globular proteins and obtain fibres, but in contact with water due to the product $\Delta\chi_1\varphi_{H_2O}$ the effective f-parameter attains at a high rate its supercritical value, and the
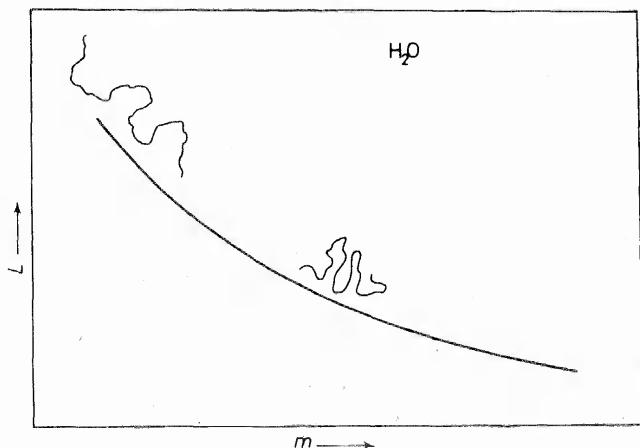
Figure 16. The Fisher diagram for proteins. *L* denotes linear dimensions which increase on decrease of the effective *f*-value. *m*—Fraction of hydrophobic units in the chain. Above the regression curve the corresponding conformations are schematically presented

resulting internal entropic stress may be sufficient not only to produce severe contraction of the fabric but even its 'annihilation'.

(ii) Under some flow conditions one observes pulsations which are ascribed to 'rheological anomalies' of polymer solutions. However, under conditions close to turbulence all can be explained by periodic binodal deformations, this time a negative feedback being provoked in the system. Due to turbulence some chains start to uncoil and fall out of solution; the forming of a smooth cluster of molecules extinguishes the turbulence, and the corresponding local region of solution returns to the unperturbed state. which is followed by the back dissolution of the fluctuation induced. This is illustrated by *Figure 17* which needs no further comments.
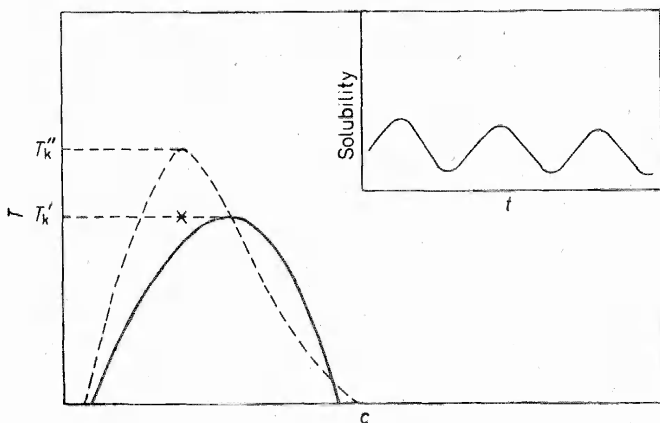

Figure 17. The interpretation of flow pulsations in terms of 'binodal deformation'

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6.2 Orientational crystallization of concentrated flexible chain polymer solutions

This case is very similar to that discussed above for fibroin, the only difference consisting in the fact that only simple uncoiling takes place, without intramolecular transitions and additional fixation due to hydrogen bonds. Since the orientational crystallization was discussed in more detail in a special paper presented at this Symposium[60], I shall remind you just of the main items.

In any external field that uncoils and orients the macromolecules at some intermediate field strength a competition begins between mono- and multi-molecular nucleation, the rate of both being given by a formula of the usual type:

$$\dot{N} = N_0 \exp\left(-\Delta F^*/kT\right) \tag{8}$$

the free energy term ΔF^* taking into account the degree of molecular orientation induced by the field. If one plots ΔF^* as a function of molecular orientation (*Figure 18*) one can see that there exists some critical orientation
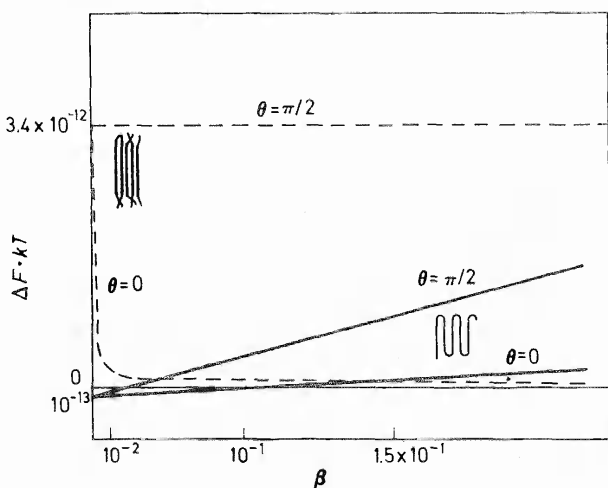

Figure 18. The dependence of the nucleation energy on orientation with regard to the stretching field (orientation angle θ) and on the mode of nucleation (schematized near the corresponding curves). β—Degree of coiling; when β tends to unity, f tends to zero

at which the formation of multimolecular nuclei becomes preferable. Turning from orientations to the fields producing them we may state that at intermediate field strength the 'non-thermodynamic' mechanism of Zachmann will act leading to formation of large loops and irregular folding; however, at still higher fields the general thermokinetic equivalence principle must lead to the possibility of coexistence of three phases (*Figure 19*). Then the fate of the growing crystals will depend on the position of nucleation on
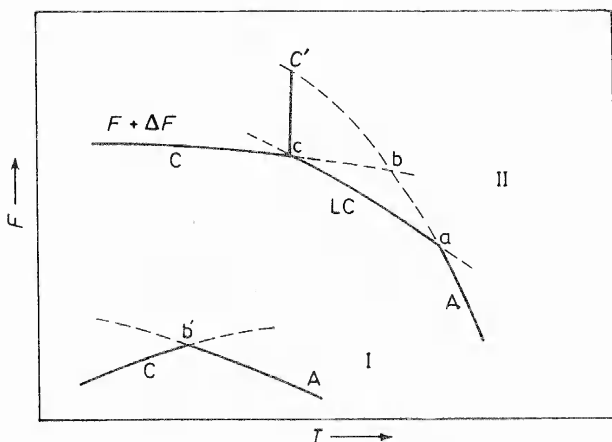
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Figure 19. The analysis of orientational crystallization with aid of an F–T diagram. For details see text, for notation see *Figure 15*

the free energy–temperature diagram. Nucleation from the nematic state will lead inevitably to extended chain crystals while the less probable nucleation from the metastable isotropic state will still supply the system with folded chain crystallites. The energy difference between the nucleation points C' and C corresponds to the ΔF^* differences in *Figure 18* for the same degrees of orientation. One more nucleation type of the 'unperturbed' origin (point b' on *Figure 19*) may occur if due to crystallization and subsequent local stress relaxation some parts of the solution become unstretched.

All three types of crystals may in principle, be observed by means of low angle x-ray scattering. The coexistence of folded and extended chain crystals is revealed readily by the fact that the average length of crystallites (calculated in the usual manner) *exceeds* the length of the large periods.

Processes of the nature discussed can play a part both in melts and solutions, the general treatment being the same, for a concentrated solution is just a swollen or diluted melt. Of course there are some minor differences, such as ejection of solvent in stretched solutions, the shifts of transition points due to dilution [in reality the $(F + \Delta F)$–T diagrams should be three-dimensional, the third axis being kept for concentration] but all these particularities are essentially unimportant corrections to the general picture.

Experimental evidence for extended chain crystallization under stretch or shear is provided by Porter's[61] and Pennings's[20, 21] studies. as well as by some other data. Very characteristic is the fact that Pennings obtained from stirred solutions polyethylene films with tensile strength as high as 100 kg mm^{-2} and with a yarn-type morphology. i.e. strongly fibrillated. Hence. one can again see the striking similarity in behaviour of essentially oriented films of rigid and flexible chain polymers both displaying properties of a solid nematic crystal.

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7 CONCLUDING REMARKS

The advantages of the thermokinetic approach to structural processes in polymers as compared to the purely thermodynamic or purely kinetic consists not only and not so much in the fact that it allows us to describe conveniently or to predict the behaviour of a complex polymer system subjected to different kinds of influences. More important, from my point of view, is the possibility of interpreting at the same time processes which would seem very different (spontaneous ordering at subcritical f values and formation of ordered structures in external fields) or morphologies (liquid crystalline systems formed by rodlike macromolecules and by flexible chain block copolymers)—in other words, to reduce them to a 'common denominator', which was, strictly speaking, proposed to the author to do in this lecture. This 'common denominator' is represented by the equivalence principle; its use allows us to avoid complicated mathematical formalisms and to reduce different modes of growth of organized structures in polymeric solutions to classical variants (playing the role of lemmas) elaborated by Flory and his school and by DiMarzio. Such a 'reduction principle' is a natural consequence of the equivalence principle. and if in cases of common systems the expediency of its application may be disputed, in the case of polymers with their many-level structural organization the convenience of this principle is unquestionable.

Together with the thermokinetic approach I used widely the concept of diphility. The inherent or explicit diphility are responsible practically for all the types of ordering in solutions or gels that were included in the programme of this Symposium. The part diphility plays in the phenomena of intra- or intermolecular ordering was discussed in sufficient detail and hardly needs additional comments. As to nucleation phenomena, the diphility equally may be either a hindrance for them (as, for instance, in case of PVA), or can promote crystallization. One should note, however, that in solutions and/or gels the nucleation phenomena are frequently complicated by the relative autonomy of different levels of the structural organization. Hence even the term 'nucleation' itself needs to be used with care. and it is necessary to define accurately the nucleation of what particular structure is discussed.

Significant in this respect are the phenomena of the 'kinetic memory' (see for example Ref. 62) which we met already when considering the collapse and restoration of spherulites. However, if in the cases mentioned above the presence of the solvent was necessary to stabilize the spherulites, now I refer to common systems, for instance, solutions of polypropylene in decalin. On repeated melting–crystallization treatment the crystallization rate (and, consequently, the primary nucleation rate) gradually increases, attaining at the fifth cycle a value approximately five times higher than the rate during the first crystallization. After this the rate changes no more, and the spherulites melt 'normally' but reappear on cooling in the same places, wholly restoring their size and internal morphology.

This result was interpreted as the persistence of 'stocks' of spherulites: the chains forming the spherulitic radii and the radii themselves retain after the fifth treatment their spatial distribution, so that the melting process was located only at the lower level of the structural organization, namely, the

crystallites. But the persistence in an implicit form of the higher levels hindered the diffusion controlled disordering of the chains forming the crystallites; hence the nucleation also was non-diffusion controlled and the respective activation energy was consequently very low. Of course this habit is also of a thermokinetic nature, the increase in temperature in the melting thermostat or the prolongation of time of incubation leading to the 'effacement' of memory, i.e. to degradation of the stocks.

It is of interest that the autonomy of levels once occurring in solution or melt persists to some extent also in the solid polymer, the kinetic memory being transformed into a 'genetic' one: again, in definite time–temperature ranges even at relatively high elongations (400 to 500 per cent) one can still observe correlation regions resembling the interspherulitic boundaries, though the spherulites themselves were long ago transformed into macrofibrils with a quite different internal structure[63].

In the solutions the presence of many levels predetermines transitions proceeding in opposite directions of the type discussed in Section 4; correspondingly, the nucleation of one type of ordered structures may proceed as a result of degradation of another type or level of organization. In combination with diphility this leads to a great abundance of different ordered morphoses in solutions: using Flory's formalism (connected with free energies) one can take into account the change of free energy on variation of solvent and/or temperature in terms of χ_1 and the related parameter f and then with aid of $F-T$ diagrams *reduce* this variety of morphoses to the ordinary polymorphism treated, for instance, in Mandelkern's monograph[7]. It is remarkable that in his analysis of polymorphism Mandelkern uses $F-T$ diagrams having the same appearance and the same physical sense as, for example, *Figure 19.* However, there is no reason to be astonished: the nucleation in presence of an external field is not simply 'reduced' to polymorphism but creates a kind of *topological* polymorphism in the true sense of the word. As was shown, this polymorphism due to external fields is possible in cases of amorphous polymers also: however, the stabilization of ordered morphoses in the absence of ordering interactions with the solvent is hardly possible; on the contrary, in crystallizable polymers the parallel packing of extended chains is fairly stable, the energy 'pumped over' from the external field being compensated for by the heat of crystallization.

Thus, from the thermokinetic viewpoint the behaviour of liquid and three-dimensional crystals, at least during the formation of corresponding phases, is of an essentially similar type—which, strictly speaking, is just what one should expect from phase transitions similar in order.

One more contribution to the 'common denominator' is provided by the structon concept. The introduction of higher order structons allows us to encompass within the frame of the equivalence principle the behaviour of block-copolymers (see p. 136–137). Moreover it accentuates the 'polymorphic' treatment, especially in cases of phase reversal as discussed by Gallot[51]. Finally one should once more mention the very likely similarity in behaviour of simple tactoids and anisometric aggregates of homodisperse blocks.

I avoided in this lecture a detailed discussion of polymer complexes though implicitly this problem was treated in Section 5. It should be mentioned that complexes discussed by Liu in his main lecture[13] and also in the paper Ref. 64

may be equally interpreted either as nuclei of ordered structures or as interactions leading to mutual crystallization hindrances but increasing the solubility of mixed systems. Finally, the specific complex formation considered in the main lecture of Chapman[65] being obviously connected with effects of diphility shows that selective interaction can produce not only organized structures but also a specific sort of 'organized behaviour' (the membranes acting as triggers). This aspect of macromolecular interactions in solutions connected with the teinochemical principle gives a basis for the incorporation of a whole system of feed-backs in polymeric ensembles and, correspondingly, for the elaboration of molecular cybernetics (see Ref. 66 though the term belongs to Ch. Sadron).

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