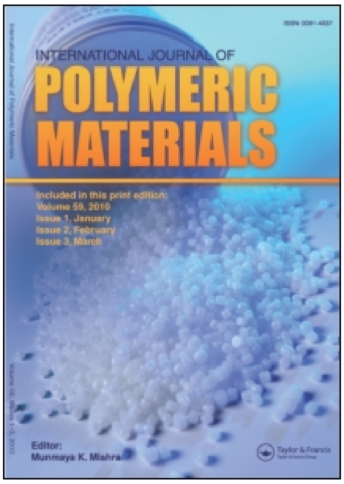

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Mechanisms of Orientation of Polymer Liquid Crystals (PLCs) in External Fields

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We analyze existing theories of behavior of polymer liquid crystals (PLCs) in external fields such as electric or magnetic. Against this background, we recall a fairly general theory of PLCs [77] and extend it to include effects of the external fields. We consider in particular phase transitions that PLCs undergo. In some cases the changes are qualitative only. However, we also observe significant quantitative modifications of phases caused by the presence of the fields.

Keywords: Polymer liquid crystals; liquid crystal orientation; electric fields; magnetic fields; phase transitions; statistical mechanics

1. INTRODUCTION

To begin with, we need to recall four important facts noted in [1]:

(i) Liquid Crystals (LCs) can be divided into monomer LCs (MLCs) and polymer LCs (PLCs).
(ii) There is a variety of phase structures of LCs, including nematic, cholesteric, and a number of smectic phases; see Section 1.6 in [1]. There is no basic difference between the phases formed by MLCs and PLCs. However, because of the connectivity between segments in PLCs, the same phase such as nematic in an MLC and in a LC-rich region in a PLC would respond differently to variations in

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temperature, composition, *etc.* The types and strength of interactions are also different, in spite of the phase similarity.

(iii) Essential for the understanding of PLC materials is the anisotropy of molecular shapes – which causes anisotropy of macroscopic properties.

(iv) Common to all LCs is the fact that the molecules are oriented *approximately* parallel to a preferred axis in space called *director.*

The anisotropy is usually enhanced by external fields, such as electric, magnetic or shear fields. Given the scope of the present volume, this first article provides some concepts useful for understanding the behavior of PLCs in electric and magnetic fields. The following papers include extensive experimental evidence on various aspects of PLC behavior under field imposition.

Clearly a *measure* of anisotropy will be useful. One such measure is provided by the so-called order parameter or anisotropy factor s defined in [1]. However, other measures are also in use. Therefore, below we shall often speak about the *extent* of *orientation* of PLC chains, without a commitment to a specific measure. When needed, and following customs established in various areas, we shall also apply specific measures of the anisotropy.

There exist a paralellism in the behavior of anisotropic macromolecules in magnetic and electric field in fluid phases. At thermal equilibrium and under a field, a partial orientation takes place. In magnetic fields we have the *Cotton-Mouton* effect such that the extent of orientation is proportional to H^2, where H is the field intensity. Analogously in the electric fields we have the *Kerr effect,* proportional to E^2, where E is now the electric field intensity. There is extensive literature on both effects, but mostly confined to MLCs [2–8].

Let us consider both proportionalities in somewhat more detail, first confining ourselves to MLCs. An MLC molecules can be represented by a rigid rod. Assume that the system of such rods obeys the Boltzmann statistics; for a discussion of this statistics see for instance Section 3.4 in [9]. Then the orientation parameter β in the magnetic field is given by [10]

$$\beta = (\chi_{//} - \chi_{\perp})H^2/kT \tag{1}$$

Here the difference $\chi_{//} - \chi_{\perp}$ of the absolute susceptibilities parallel and perpendicular to the rod axis describes anisotropy of the molecule; k is Boltzman constant and T is thermodynamic temperature. While

Eq. (1) pertains to MLCs, Maret *et al.* [8] have considered a *cluster* of hard rod molecules and found that in this case also β is proportional to the r.h.s. of Eq. (1). Going still further, the same authors used the Kratky-Porod model [11] to represent a *longitudinal* PLC. Such a PLC consists of rigid (LC) and flexible sequences, with both kinds of sequences located in the main chain and oriented along the chain backbone [1]. Maret *et al.* [8] have obtained the result

$$\beta = (2P/l_0)(\chi_{//} - \chi_{\perp})H^2/kT \tag{2}$$

where P is persistent length and l_0 is the length of one monomer; both P and l_0 characterize the flexibility of the macromolecule.

While the theory of behavior of PLCs in magnetic and electric fields is less developed than that for MLCs, some experimental evidence and theoretical results have been gathered [12–32]. It turns out that for real PLCs the linear relation between β and H^2 predicted by Eq. (2) is only an approximation. We shall discuss this problem in some detail in Section 5. For the time being let us note that the extant theories of the Cotton-Mouton and Kerr effects predict a monotonous increase of local orientation with increasing intensity of the field. This works well for MLCs, but in PLCs we have phase transitions such as isotropic $\mapsto$ nematic (or smectic), isotropic $\mapsto$ cholesteric, and/or cholesteric $\mapsto$ nematic or smectic [33].

Most theories of PLCs focused on the question how *internal* interactions affect phase transitions. However, some results for PLCs in *external* fields exist, and will be discussed in the following section.

2. A SHORT REVIEW OF EXTANT THEORIES

The Flory theory of liquid crystallinity in systems containing longitudinal PLC macromolecules was formulated in 1956 [34, 35]. Flory considered a system of linear semiflexible PLC chains in which each macromolecule consists of flexible and LC sequences. The former can coil and have internal conformational entropy. The latter are represent by rigid rods. Subsequently, the theory was amplified by Flory, his colaborators and students, for lyotropic and thermotropic systems [36–50].

Flory used the *lattice* approach to construct the distribution function of the system. As discussed in some detail in [48], he developed an ingenious procedure allowing placing LC sequences at any angle to the lines of the lattice; see Figure 1. The number of such combinations allows to determine the probability of a state of the system. On this basis we can derive thermodynamical functions such as entropy, the Gibbs or the Helmholtz function. Subsequently by appropriate optimizations one can obtain the phase equilibrium parameters.

In [51] de Gennes proposes a *nonlattice* approach. A system is represented by a three-chain cell, with mutually perpendicular end-to-end distances, as shown in Figure 2. Chains constituting a cell are freely-jointed chains of Kuhn segments. Kuhn [52, 53] and later Kuhn and Grün [54] have shown how a real polymer chain can be represented by an equivalent freely-jointed (also called random flight) chain. The basic units are sequences consisting of several bonds each. Given a sufficient number of bonds per sequence, the direction of a sequence will be independent of the direction of the preceding sequence. Mathematically, this is the drunk (random) walk problem, mentioned here also in Section 3, and explained in some detail in

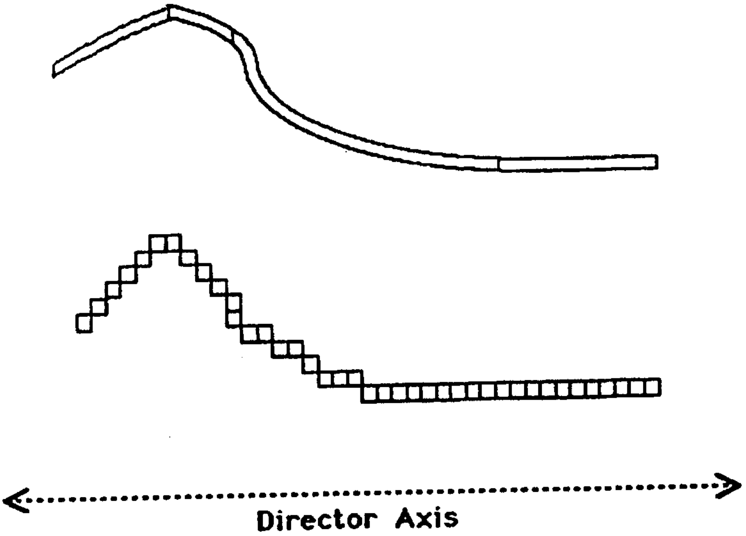

FIGURE 1 A four-sequence part of the system chain (top) and its lattice representation (bottom). The third sequence from the left is flexible; the remaining ones are liquid crystalline. The first sequence from the left consists of six submolecules. The sequences 1 to 3 from the left deviate from the system director axis. The fourth sequence is parallel to the director axis (after [48]).

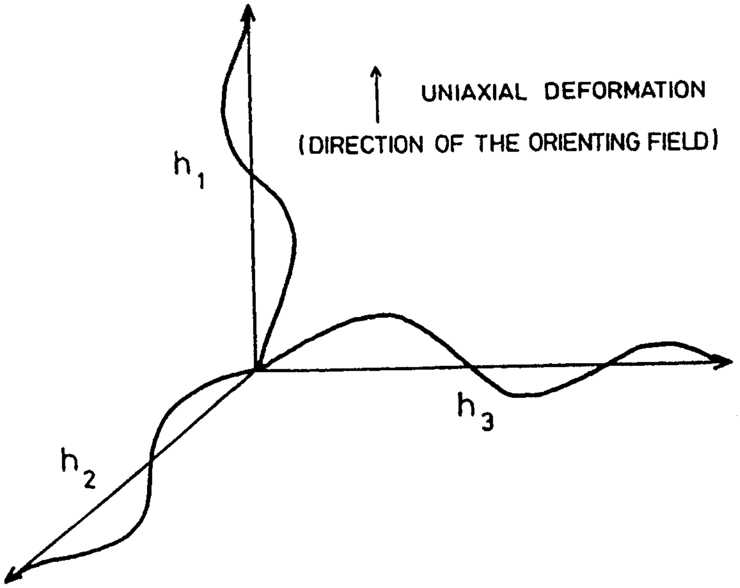

FIGURE 2 Three-chain cell representation of a polymer network. Chains end-to-end vecors $\boldsymbol{h}_1$, $\boldsymbol{h}_2$ and $\boldsymbol{h}_3$ are mutually perpendicular. The director axis is induced by the uniaxial deformation of the system (after [58]).

Section 12.2 of [9]. This leads to the Gaussian distribution of probabilities of the chain end-to-end distances. The average of the square of the end-to-end distance for the chain turns out to be proportional to the degree of polymerization r (not to r^2); see for instance Section 6.5 in [9]. However, potential orienting interactions between segments are allowed. The distribution of chain segment orientations ρ is obtained by requiring that the Helmholtz function A functional with respect to ρ becomes the minimum. Here the distribution ρ is the probability density. For a discussion of probability functions see for instance again Section 4.3 in [9]. Other conditions result from border conditions imposed on the system. The theory was considered further by Jarry and Monnerie [55] and by one of us in [56 – 60]. It turns out that the nematic-like phase of the system is induced by uniaxial deformation of the system [55 – 60]. Some results for the system with nematic-like phase induced by an external electric field have been reported [59, 60].

The well-known Kratky-Porod model of the persistent chain has been adapted by several authors to deal with PLCs [61 – 63]. In the adaptation the chain stiffness is enforced by orienting potential forces characteristic for liquid crystallinity. The model gives some interesting results for biaxial interactions and predicts cholesteric phases in PLCs.

As noted at the start of this Chapter, properties of PLC materials depend strongly on the molecular structures of the macromolecules that form them. The structures can be divided into several clases [1, 64], including networks and three-dimensional conic PLCs. As already noted above, the most frequent are longitudinal PLCs.

One of the parameters describing a liquid crystal phase structure is the *order parameter* s which is defined as the average $\langle P_2 \rangle$ over LC orientations of the second Legendre polynomial [1, 33, 64]. In the following we shall be primary concerned with the behavior of s. Therefore, to understand what the value of s are telling us, consider the following (not necessarily mutually exclusive) cases:

for all molecules exactly parallel to the director $s = 1$ (1)
for the isotropic phase (= random orientation of the molecules) $s = 0$ (2)
for nematic or smectic phases $s > 0$ (3)
for cholesteric phases $s < 0$ (4)

It should be noted that $s < 0$ is a necessary but not a sufficient condition for the formation of a cholesteric phase. An analogous statement applies to $s > 0$ and the formation of either nematic or smectic phases. Moreover, each cholesteric phase has a local nematic structure with the nematic axis perpendicular to the helix axis; "local" represents here the level of a single segment. We recall that PLC are hierarchical in structure, can be considered at different levels, hence ascensions and descensions in the hierarchy are important [65]. Therefore, if we define s with relation to such a nematic axis-rather than with respect to the director (= the helix axis) of the entire cholesteric phase-then we have *locally* $s > 0$.

The hierarchical nature of PLCs and the connectedness of segments have further consequences. The rigid LC sequences flock together, as do free trunks on a flowing river. However, these sequences necessarily pull with them some of the flexible sequences. Thus LC-rich *islands* are formed [66], with each island surrounded by a LC-poor matrix. Since the islands are formed by the same orientation-in-flow process, the directors of individual islands are close to each other, but not identical. Islands and related topics are also discussed by Gedde and Wiberg in Chapter 10 in [67].

Both Flory and de Gennes theories as well as latter theories involving uniaxial interactions between LC sequences [68–71] predict only the transition from $s = 0$ to $s > 0$. However, experiments [72–76] and some theoretical results for biaxial orienting interactions [61–63] suggest possibilities of other types of transition such as from $s = 0$ to $s < 0$ or from $s < 0$ to $s > 0$. This situation behooved us to formulate a new approach [77] to the PLCs theory in which all phase transitions are predictable; the model so created is described in the following section.

3. A GENERAL MODEL OF PLC SYSTEMS

The generalized theory [77] is based on a non-lattice approach. The system consists of N_{ch} semiflexible chains; the structure of a chain is shown in Figure 1. To derive the necessary equations, one uses the random walk method for the calculation of probability of a flexible part of the system; see [52–54, 78–80] or Section 12.2 in [9]. At the same time one uses the Gibbs dictribution [81] for the probability of LC particle states. The superposition of these probabilities gives a general formula for the probability of the whole PLC system. The general results in [77] are not constrained to any special type of orienting interactions between LC particles and/or with an orienting external field. Some special results are obtained for:

- chains with long flexible parts;
- induced dipole–dipole internal interactions between LC rods in the Maier-Saupe mean-field theory limit [82, 83].

In the latter case the Helmholtz function $\tilde{A}$ per particle is [77]

$$\tilde{A}/kT = u_h s(s+1)/2 - \ln f_0 + (3\kappa/2\langle n\rangle)\big[(\Lambda_x - 1)^2(1 - f_2)/2 + (\Lambda_y - 1)^2(1 - f_2)/2 + (\Lambda_z - 1)^2 f_2\big] + \text{const.} \qquad (5)$$

where u_h is a potential constant describing intensity of interactions between LC sequences and is inversely proportional to the thermodynamic temperature T [82, 83]; this is intuitively understable since higher temperatures produce more free volume and weaker interactions. κ is a parameter representing the concentration of LC sequences in the flexible part of the system. Λ_x, Λ_y and Λ_z define the symmetry deformation with respect to the presence of molecular mean field; effects of external fields on these parameters are seen in the next section in Eqs. (8) and (9). f_0 and f_2 are integral functions dependent on the orientation parameter s and on u_h; again see more in the next section. A variety of possible phases and phase transitions predicted by the theory is shown in Figures (2) and (3). The phase diagram for u_h *vs.* κ is shown in Figure (4). Inspection of Figure (4) and its comparison to Figures (2) and (3) show many possibilities of phase transitions for various pairs u_h and κ. The overall situation results from competition between energetic and entropic effects, which respectively play prevailing roles in the LC and flexible parts of PLC chains [84–88]. Thus, the objective of developing a model capable of predicting all types of phase transitions possible has been accomplished.

Discussion of Figures (2) and (3) leads to the conclusion that all types of the phase transitions in PLCs with dipole–dipole interactions are of the first order [77] in terms of the Landau classification [81]. More specifically, the typical behavior of uniparticle Helmholtz function shows that each change of s from a state in which global minima of $\tilde{A}(s)$ have the same values (equilibrium) to a state for which $\tilde{A}(s)$ has only one minimum is of the jumping type. This can be seen for

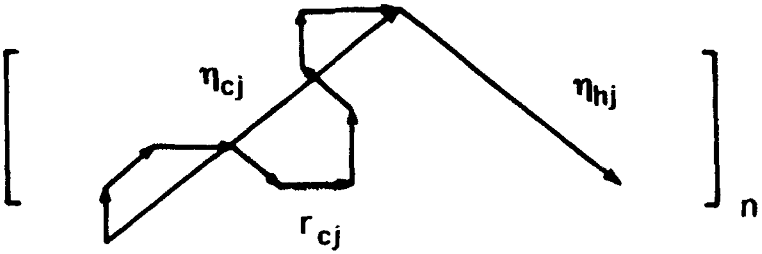

FIGURE 3 The basic element of a semiflexible PLC copolymer chain. The chain consists of n lineary copolimerized elements, so that $j = 1, \ldots, n$. The j-th element consists of flexible (coil) and liquid crystalline (rodlike) sequences. The end-to-end vectors in the j-th part are, respectively, η_{cj} for flexible and η_{hj} for LC sequences. The j-th flexible sequence consists of η_{cj} freely jointed segment vectors r_{cj}; $i = 1, \ldots, \eta_{cj}$. The length l of a segment-vector r_{cj} is the same for all segments (after [77]).

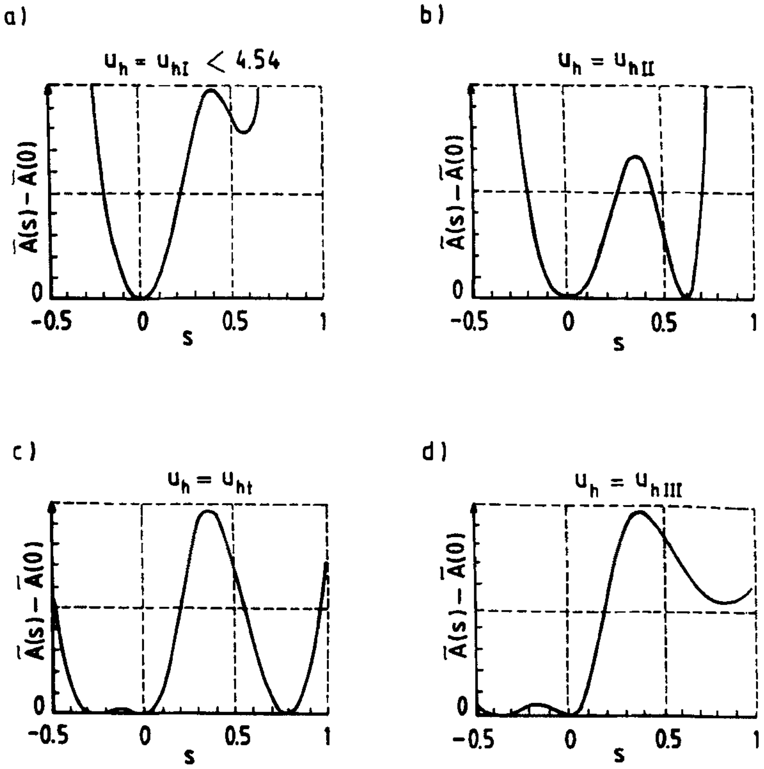

FIGURE 4 A typical behavior of the Helmholtz function $\tilde{A}$ of PLCs *vs.* the orientation parameter s for several u_h values. (a) $s = 0$ (isotropic phase), (b) $s = 0$ and $s > 0$ (isotropic-nematic or isotropic-smectic equilibrium), (c) $s < 0$, $s = 0$ and $s > 0$ (cholesteric-isotropic-nematic or cholesteric-isotropic-smectic equilibrium), (d) $s = 0$ and $s < 0$ (cholesteric-isotropic equilibrium). Values of $u_{h\,\mathrm{I}}$, $u_{h\,\mathrm{II}}$ or $u_{h\,\mathrm{III}}$, are related respectively to the values of u_h from zones I, II or III in Figure (6). $u_{h\,t}$ is the value of u_h on the three-phasic equilibrium line marked by t in Figure (6) below (after [77]).

instance in Figure (2): (a) the system is at equilibrium for $s = 0$, (b) the system is at equilibrium with two phases, one with $s = 0$ and the other with $s > 0$. A change of s from $s = 0$ to $s > 0$ is of the jump type. Precisely this means in the Landau classification that the phase transition is of the first order.

The general results of the theory [77] shortly sumarized here can be applied to PLCs in an external magnetic or electric field; see the next section.

4. THE HELMHOLTZ FUNCTION OF PLCs IN EXTERNAL FIELDS

An external electric or magnetic field can modify the types of phase transitions. This has to be kept in mind when extending the theory described in the previous section by inclusion of external fields. Our extension [89] is based on assuming the following form of the potential energy of interaction between an LC dipole and an external orienting field:

$$u(\vartheta)/kT = -u_{\text{ex}} \cos\vartheta \tag{6}$$

Here ϑ is the angle between the dipole vector of the LC molecule and the direction of the field, while u_{ex} is the intensity of the external field in kT units. Using the energy defined by Eq. (6) in conjuction with the Eq. (5) for $\tilde{A}$, we obtain [89] the uniparticle Helmholtz function of the form:

$$\begin{aligned}\tilde{A}/kT = {} & u_h s(s+1)/2 - \ln f_0 + (1/2\langle n\rangle)(\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2) \\ & + (3\kappa/2\langle n\rangle)\left[(\Lambda_x - 1)^2(1-f_2)/2 + (\Lambda_y - 1)^2(1-f_2)/2 \right. \\ & \left. + (\Lambda_z - 1)^2 f_2\right] + (3\kappa/2)(\Lambda_z - 1)^2 f_1^2 + \text{const.}\end{aligned} \tag{7}$$

where

$$\Lambda_z^2 = \left[3\kappa(f_2 + \langle n\rangle f_1^2) + 1\right]/(\kappa+1) \tag{8}$$

$$\Lambda_x^2 = \Lambda_y^2 = \left[3\kappa(1-f_2)/2 + 1\right]/(\kappa+1) \tag{9}$$

Here κ is the same concentration parameter as in Eq. (3), while $\langle n\rangle$ is the average number of LC sequences per chain. The integral functions f_0, f_1 and f_2 are given by:

$$f_0 = \int_{-1}^{1} \exp(u_{\text{ex}} z + 3u_h s z^2/2)\,dz \tag{10}$$

and

$$f_n = \int_{-1}^{1} z^n \exp(u_{\text{ex}} z + 3u_h s z^2/2)\,dz/f_0 \tag{11}$$

where $n = 1$ or 2.

The Helmholtz function $\tilde{A}$ in Eq. (2) involves two mechanisms of orientation of LC sequences:

- orienting interaction of LC with molecular mean field;
- orienting interaction of LC with an external field.

The first effect stems from internal dipole–dipole interactions between LC sequences. The parameter u_h describes the intensity of these interactions. The parameter u_{ex} provides information on the intensity of external (magnetic $u_{ex} = H$, electric $u_{ex} = E$) fields which interact with the LC particles *via* the potential energy given by Eq. (6). As discussed above in Section 3, dipole–dipole LC interactions determine the phase transitions in the system. In the next section we shall show how the presence of an external orienting field affects this situation.

5. PHASE TRANSITIONS IN EXTERNAL FIELDS

A variety of possibilities of modification of phase transitions by field imposition is illustrated in Figures (1 – 5) [89]. For comparison in Figure (1a) we show a plot of $\tilde{A}$ *vs.* the order parameter s for the system in the *absence* of the external field, that is for $u_{ex} = 0$. The function $\tilde{A}(s)$ has one global minimum for $s = 0$, so that the system at equilibrium is in the isotropic phase. In Figure (1b) we see the plot $\tilde{A}(s)$ for the same system but in the *presence* of an external field ($u_{ex} > 0$). Now the function has one global minimum for $s > 0$. The change of s from zero to a positive value is continuous while u_{ex} increases also from zero to a positive value. In terms of the Landau classification [81], and as discussed at the end of the Section 3, this means that the phase transition isotropic-nematic (or isotropic-smectic) is *not* of the first order.

A plot of $\tilde{A}(s)$ is shown in Figure (2a) for the system in the isotropic phase in the absence of an external field ($u_{ex} = 0$), but for different values of κ and u_h than in Figure (1a). There exists a variety of parameters κ and u_h for which the isotropic phase can be realized; see against the phase diagram in Figure (6). When an external field is switched on, the isotropic-to-cholesteric ($s < 0$) phase transition is observed; it is not of the first order as can be seen in Figure (2b).

In Figures (1) and (2) we see the possibility of qualitative changes of the phases in the system phase caused by an external field. In some cases the change is *quantitative* only, as in Figure (3). The presence of the field in Figure (3b) produces an increase of the value of s for which $\tilde{A}(s)$ has a minimum, this in comparison with the analogous value of s in the absence of the external field in Figure (3a).

However, with a further increase of u_{ex} values we can observe significant *qualitative* modifications of the system phases. This situation is illustrated in Figure (4b), where for a value of $u_{ex} = u_{exb}$ we observe the

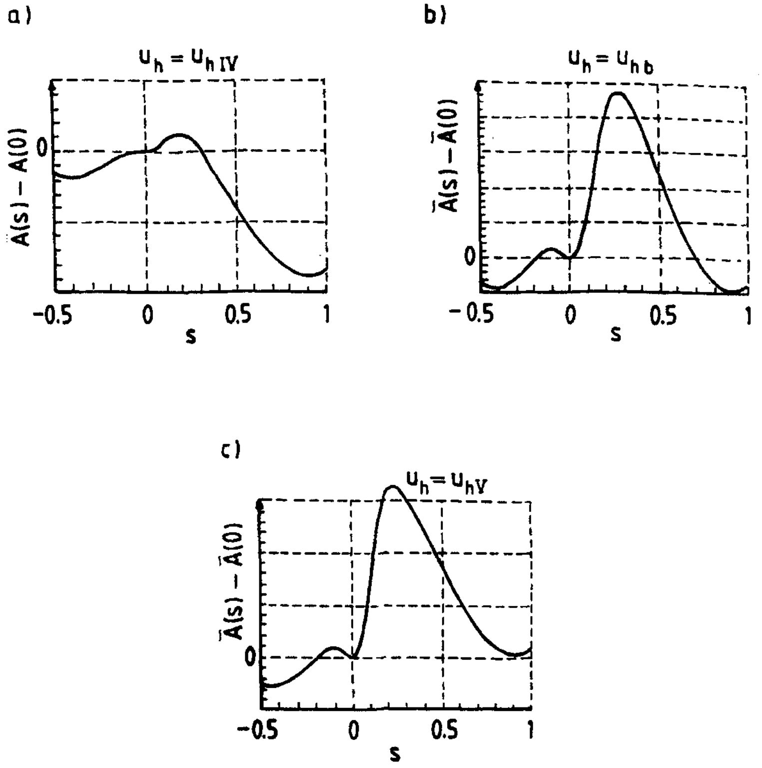

FIGURE 5 A typical behavior of the Helmholtz function $\tilde{A}$ of PLCs *vs.* the orientation parameter s for u_h values different than those in Figure (2). (a) $s > 0$ (nematic or smectic phase only), (b) $s < 0$ and $s = 0$ (cholesteric nematic or cholesteric smectic equilibrium), (c) $s < 0$ (cholesteric phase only). As in Figure 2, $u_{h\ \mathrm{IV}}$ and $u_{h\ \mathrm{V}}$ are related to zones IV and V in Figure (6). $u_{h\ b}$ is the value of u_h on the biphasic equilibrium line marked by b in Figure (4) below (after [77]).

first order phase transition from $s > 0$ (nematic or smectic) to $s < 0$ (cholesteric). A further increase of u_{ex} can lead to one cholesteric phase only. Thus, the external field presence can modify PLCs phases from nematic (smectic) in Figure (4a), *via* nematic (smectic)-cholesteric equilibrium in Figure (4b), up to a cholesteric phase alone in Figure (4c).

The possibility of induction of *subphases* by an external field within one phase of the system is illustrated in Figure (5). In (5a) the system is in the absence of an external field and forms a cholesteric phase with $s < 0$. An increase of u_{ex} values up to $u_{\mathrm{ex}} = u_{\mathrm{exb}}$ leads to the separation of one cholesteric phase into two, highly and weakly ordered, with

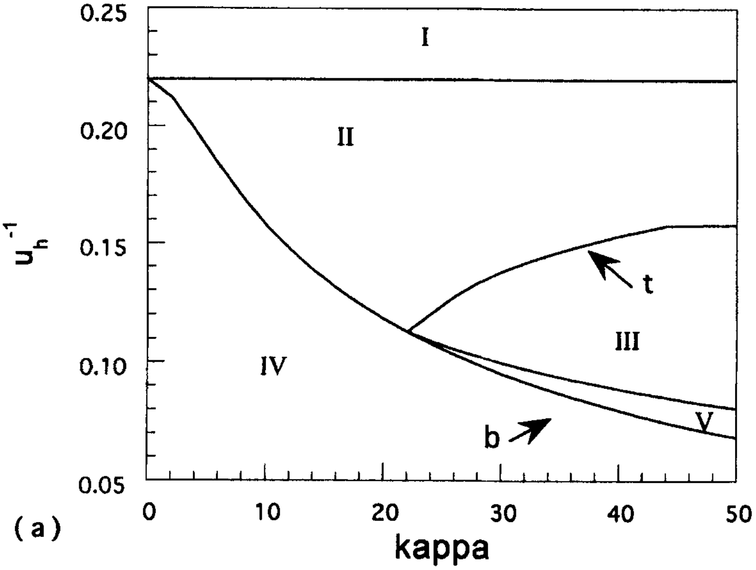

FIGURE 6 Phase diagram for a PLC system in terms of the parameters u_h^{-1} and κ. In the zone I the parameter $u_h < 4.54$ and the system is in equilibrium for $s = 0$ (isotropic). In zones II–V the parameter $u_h > 4.54$ and the system is in biphasic equilibrium with $s = 0$ and $s > 0$ (isotropic-nematic or isotropic-smectic) in the zone II, and in biphasic equilibrium with $s = 0$ and $s < 0$ (isotropic-cholesteric) in the zone III. In the zone IV the system is at equilibrium with $s > 0$ (nematic or smectic) and in the zone V the system is at equilibrium with $s < 0$ (cholesteric) only. The curve t represent the three-phasic cholesteric-isotropic-nematic (or smectic) equilibrium, the curve b biphasic cholesteric-nematic (or smectic) equilibrium (after [77]).

different values of s. This is illustrated in Figure (5b). A further increase of u_{ex} leads to the disappearance of the highly ordered phase, while the weakly ordered cholesteric phase remains. We recall Rule 5 of formation of hierarchical structures [65]: assembling entities in a specified way can achieve properties which a system is of un-assembled entities does not have. PLCs are hierarchical, as discussed in particular by Sawyer and Jaffe [90] on the basis of experimental evidence. We see here how the Rule applies: the same entities produce two distinct cholesteric phases. Our approach is quantitative, while in the literature one find various discussions of "molecular architectures"; no generally accepted definition what that term means exist.

Inspection and our discussion of Figures (1) – (11) show a wide variety of modification of PLCs phases by an external orienting field. The

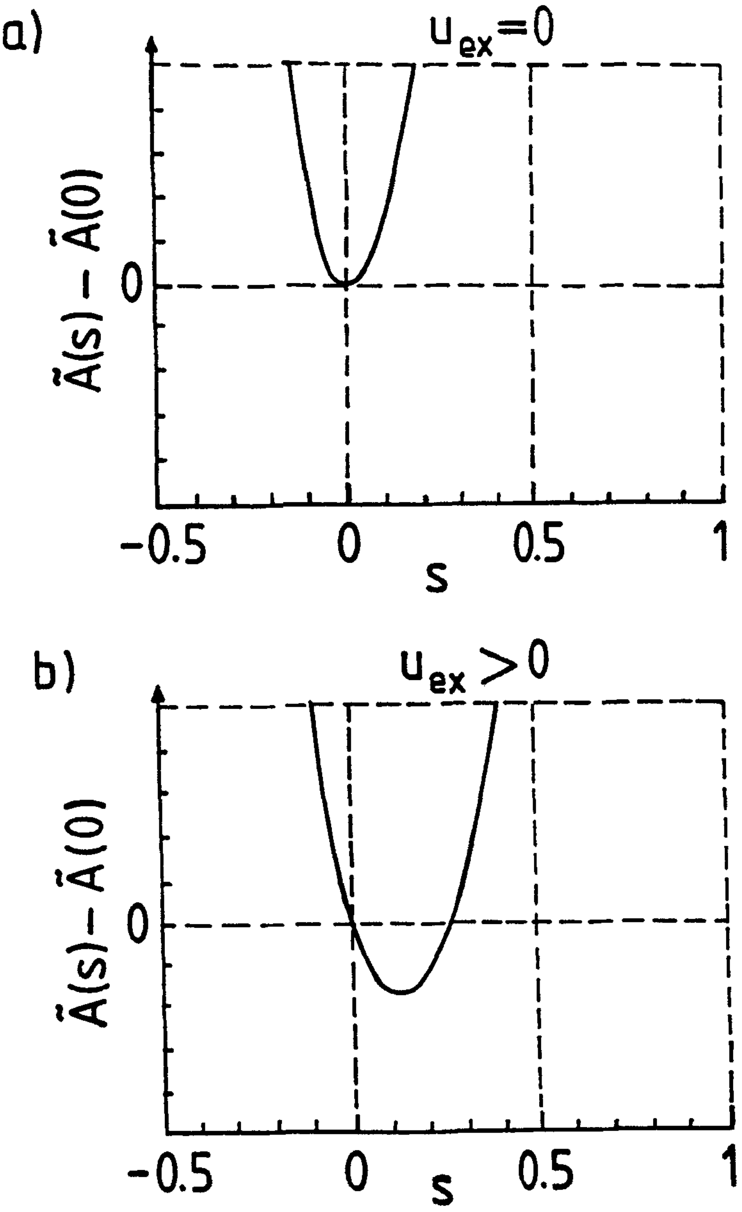

FIGURE 7 A typical behavior of the Helmholtz function $\tilde{A}$ of PLCs *vs.* the orientation parameter s. (a) in the absence of an external field, $u_{ex} = 0$, the system is at equilibrium for $s = 0$ (isotropic); (b) in the presence of an external field, $u_{ex} > 0$, the system is at equilibrium for $s > 0$ (nematic or smectic). The phase transition from (a) to (b) is induced by the external field and in the Landau classification is not of the first order (after [89]).

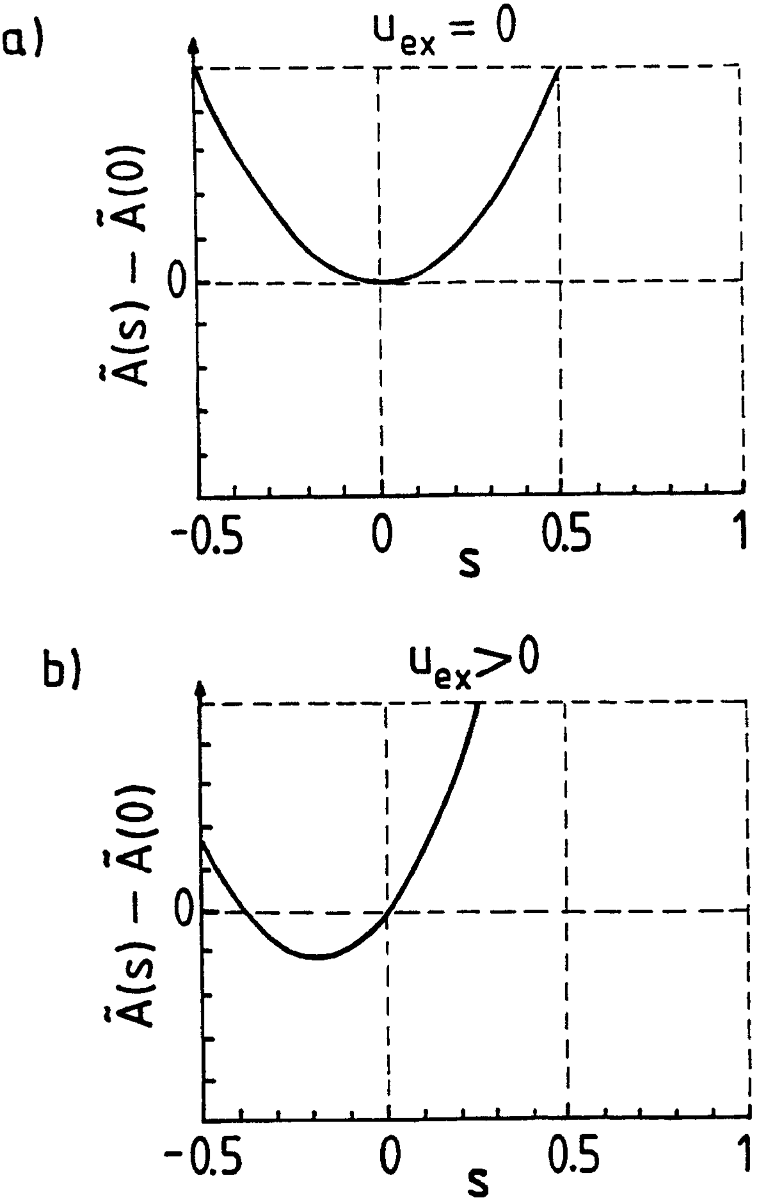

FIGURE 8 A typical behavior of the Helmholtz function $\tilde{A}$ of PLCs *vs.* the orientation parameter s: (a) in the absence of an external field the system is at equilibrium for $s = 0$ (isotropic); (b) in the presence of an external field the system is at equilibrium for $s < 0$ (cholesteric). The phase transition from (a) to (b) is induced by the external field and is not of the first order (after [89]).

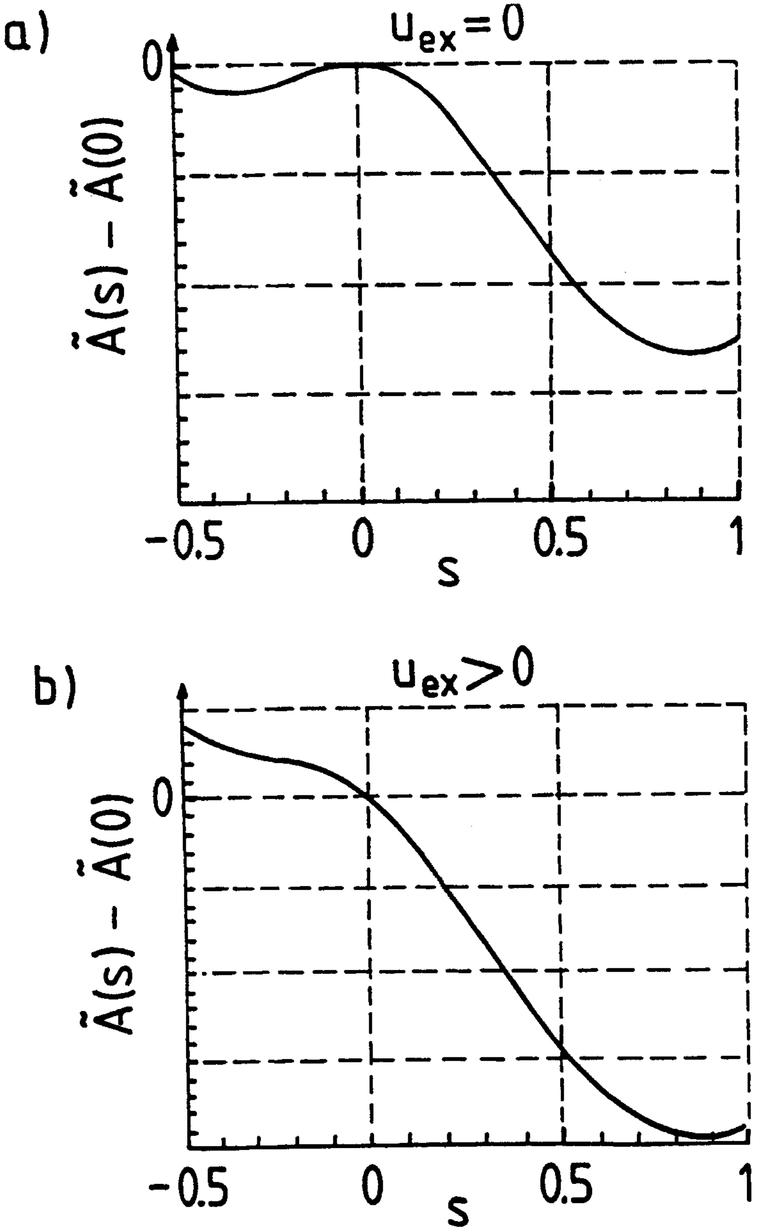

FIGURE 9 A typical behavior of the Helmholtz function $\tilde{A}$ of PLCs in nematic or smectic equilibrium *vs.* the orientation parameter s: (a) in the absence of an external field; (b) in the presence of an external field. In both cases $s > 0$, so that in this case an external field does not induce a phase transition (after [89]).

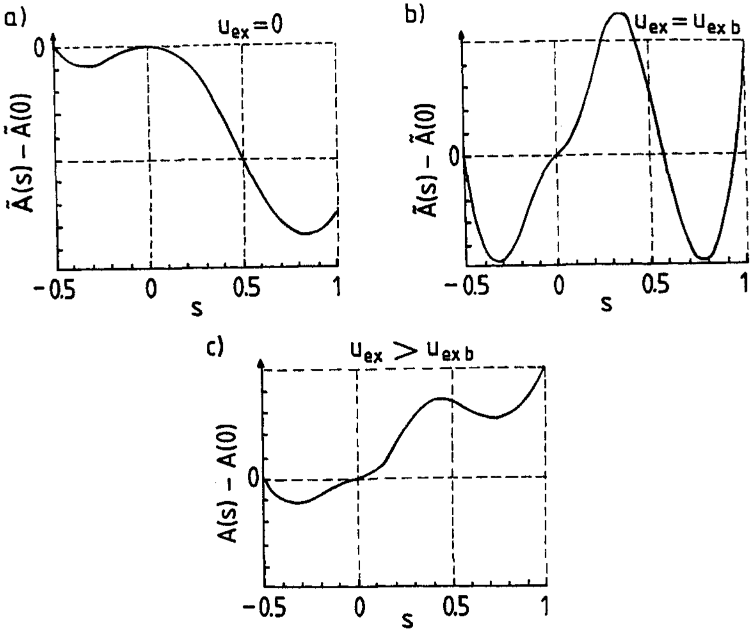

FIGURE 10 A typical behavior of the Helmholtz function $\tilde{A}(s)$ of the same PLC as in Figure 3, but for higher value of u_{ex}: (a) in the absence of an external field the system is in equilibrium for $s > 0$ (nematic or smectic); (b) in the presence of an external field for the value $u_{ex} = u_{exb}$, $s < 0$ and $s > 0$, hence we have biphasic cholesteric-nematic or cholesteric-smectic equilibrium; (c) for $u_{ex} > u_{exb}$, $s < 0$ and the system is in the cholesteric phase. The nematic (smectic)-to-cholesteric phase transition is induced by the external field and is of the first order according to the Landau classification (after [89]).

modification of an ordering leads to changes of the orientation order parameter s as a function of u_{ex}. The function is *not* so simple as that discussed in Section 1 where orientation parameter is simply proportional to the square of the external field intensity. In consequence, the theory presented here predict that PLCs systems often are *not* under control of the Cotton-Mouton or Kerr equations, the fact confirmed by experiment (see again discussion in Section 1). Thus, and in contrast to earlier approaches the theory presented here provides a fairly realistic interpretation of the behavior of PLCs in external orienting fields.

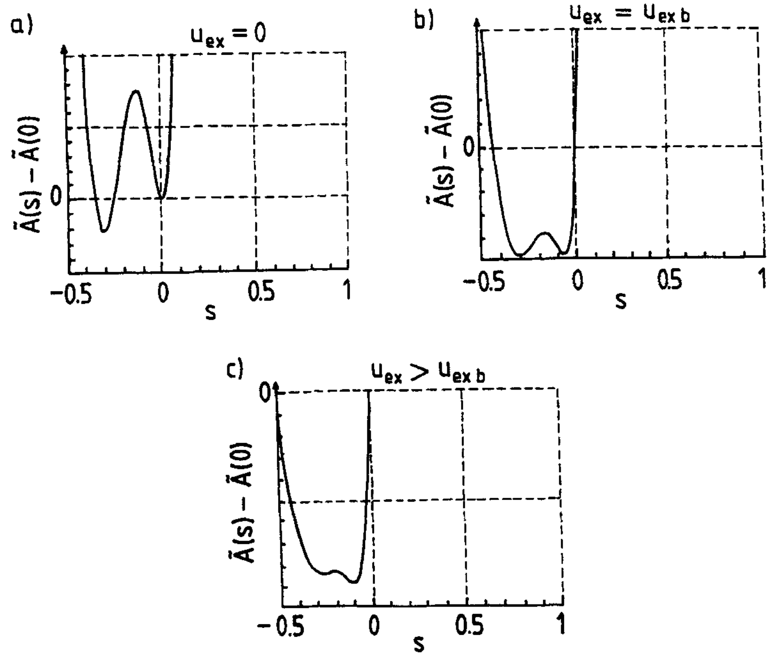

FIGURE 11 An illustration of separation of a cholesteric PLC phase into two phases shown as a plot of the Helmholtz function $\tilde{A}$ *vs.* the orientation parameter s: (a) in the absence of an external field we have $s < 0$ (cholesteric phase only); (b) for $u_{ex} = u_{exb}$ the system is at equilibrium for two values of $s < 0$ (cholesteric highly oriented and cholesteric weakly oriented); (c) for $u_{ex} > u_{exb}$ we have $s < 0$, but only the weakly oriented phase remains. The phase transition highly-to-weakly oriented is induced by the external field and is of the first order in the Landau classification (after [89]).

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References

[1] Brostow, W. (1992). Chapter 1 In: *Liquid Crystal Polymers: From Structure to Applications* (Collyer, A. A., Ed.). Elsevier Applied Science, London-New York.

[2] Freederics, V. K. and Zolina, V. V. (1931). *Z. Kristalogr.*, **79**, 255.

[3] Freederics, V. K. and Tsvetkov, V. N. (1934). *Phys. Z. Sowietunion*, **6**, 490.
[4] Freederics, V. K. and Tsvetkov, V. N. (1935). *Acta Physicochim. URSS*, **3**, 879.
[5] Freederics, V. K. and Tsvetkov, V. N. (1935). *Acta Physicochim. URSS*, **3**, 895.
[6] Tsvetkov, V. N. (1937). *Acta Physicochim. URSS*, **6**, 865.
[7] Maret, G., v. Schickfus, M. and Mayer, A. (1975). *Phys. Rev. Letters*, **35**, 379.
[8] Maret, G. and Dransfeld, K. (1977). *Physica*, **86**, 1077.
[9] Brostow, W. (1979). Science of Materials, Wiley, New York (and (1985) Krieger, Malabar, FL); (1985) Einstieg in die moderne Werkstoffwisenschaft, Carl Hanser Verlag, München-Wien.
[10] Izuka, E. (1999). *Internat. J. Polym. Mater.*
[11] Porod, G. (1949). *Monatsh.*, **80**, 251.
[12] Iizuka, E. (1971). *Biochim. Biophys. Acta*, **243**, 1.
[13] Iizuka, E. and Go, Y. (1971). *J. Phys. Soc. Japan*, **13**, 1205.
[14] Iizuka, E. (1973). *Polymer J.*, **5**, 62.
[15] Iizuka, E. (1974). *Mol. Cryst. Liq. Cryst.*, **27**, 161.
[16] Iizuka, E. (1976). *Adv. Polymer Sci.*, **20**, 79.
[17] Tsvetkow, V. N., Kolomiets, I. P., Stepchenkov, A. S., Alimov, S. V., Bilibin, A. Yu. and Skorokhodov, S. S. (1989). *Vysokomol. Soedin*, **31**, 700.
[18] Tsvetkov, V. N., Andreeva, L. N., Filippov, A. P., Smirnova, G. S., Skorokhodov, S. S. and Bilibin, A. Yu. (1992). *Polymer Sci.*, **34**, 335.
[19] Tsvetkov, V. N., Tsvetkov, N. V., Andrieeva, L. N., Bilibin, A. Yu. and Skorokhodov, S. S. (1993). *Polymer Sci.*, **35**, 335.
[20] Noel, C., Monnerie, L., Achard, M. F., Hardouin, F., Sigaud, G. and Gasparoux, H. (1981). *Polymer*, **22**, 578.
[21] Sigaud, G., Yoon, D. Y. and Griffin, A. C. (1983). *Macromolecules*, **16**, 875.
[22] Esnault, P., Galland, D., Volino, F. and Blumstein, R. B. (1989). *Macromolecules*, **22**, 3734.
[23] Furuya, H., Abe, A., Fuhrmann, K., Balauff, H. and Fischer, E. W. (1991). *Macromolecules*, **22**, 2999.
[24] Achard, M. F., Sigaud, G., Hardouin, F., Weill, C. and Finkelmann, H. (1993). *Mol. Cryst. Liq. Cryst.*, **92**, 111.
[25] Schönhals, A. and Carius, H. E. (1999). *Internat. J. Polym. Mater.*, **45**, 239.
[26] Hikmet, R. A. M. (1999). *Internat. J. Polym. Mater.*
[27] Shibaev, V. P. (1999). *Internat. J. Polym. Mater.*, **45**, 307.
[28] Itoh, N. (1999). *Internat. J. Polym. Mater.*, **45**, 349.
[29] Francescangeli, O. and Simoni, F. (1999). *Internat. J. Polym. Mater.*, **45**, 381.
[30] Bunning, T. J., Korner, H. K., Ober, C. K. and Adams, W. W. (1999). *Internat. J. Polym. Mater.*, **45**, 451.
[31] Zubia, J. and Etxebarria Ecenarro, J. (1999). *Internat. J. Polym. Mater.*, **45**, 503.
[32] Shibaev, V. P. and Boiko, N. (1999). *Internat. J. Polym. Mater.*, **45**, 533.
[33] de Gennes, P. G. (1974). The Physics of Liquid Crystals, Clarendon Press, Oxford; de Gennes, P. G. and Prost, J. (1993). The Physics of Liquid Crystals, 2nd Ed., Clarendon Press, Oxford.
[34] Flory, P. J. (1956). *Proc. Royal Soc. A*, **234**, 60.
[35] Flory, P. J. (1956). *Proc. Royal Soc. A*, **234**, 73.
[36] Flory, P. J. and Ronca, G. (1979). *Mol. Cryst. Liq. Cryst.*, **54**, 289.
[37] Flory, P. J. and Ronca, G. (1979). *Mol. Cryst. Liq. Cryst.*, **54**, 311.
[38] Flory, P. J. and Abe, A. (1978). *Macromolecules*, **11**, 1119.
[39] Flory, P. J. and Abe, A. (1978). *Macromolecules*, **11**, 1122.
[40] Flory, P. J. and Frost, R. S. (1978). *Macromolecules*, **11**, 1126.
[41] Frost, R. S. and Flory, P. J. (1978). *Macromolecules*, **11**, 1134.
[42] Flory, P. J. (1978). *Macromolecules*, **11**, 1138.
[43] Flory, P. J. (1978). *Macromolecules*, **11**, 1141.
[44] Matheson, R. R. and Flory, P. J. (1981). *Macromolecules*, **14**, 954.
[45] Flory, P. J. and Irvine, P. A. (1984). *Faraday Trans.*, **80**, 1807.

[46] Flory, P. J. and Matheson, R. R. Jr. (1985). *J. Chem. Phys.*, **88**, 6006.
[47] Matheson, R. R. Jr. (1986). *Macromolecules*, **19**, 1286.
[48] Jonah, D. A., Brostow, W. and Hess, M. (1993). *Macromolecules*, **26**, 76.
[49] Blonski, S., Brostow, W., Jonah, D. A. and Hess, M. (1993). *Macromolecules*, **26**, 84.
[50] Brostow, W. and Walasek, J. (1994). *Macromolecules*, **27**, 2923.
[51] de Gennes, P. G. (1975). C. R. Hebd. *Seances Acad. Sci. B*, **281**, 101.
[52] Kuhn, W. (1936). *Kolloid-Z*, **76**, 258.
[53] Kuhn, W. (1939). *Kolloid-Z*, **87**, 3.
[54] Kuhn, W. and Grün, F. (1942). *Kolloid-Z*, **101**, 248.
[55] Jarry, J. P. and Monnerie, L. J. (1978). *J. Polymer Sci. Phys.*, **16**, 443.
[56] Walasek, J. (1988). *J. Polymer Sci. Phys.*, **26**, 1907.
[57] Walasek, J. (1990). *J. Polymer Sci. Phys.*, **28**, 1075.
[58] Walasek, J. (1990). *J. Polymer Sci. Phys.*, **28**, 2473.
[59] Walasek, J. (1992). *J. Polymer Sci. Phys.*, **30**, 401.
[60] Walasek, J. and Grela, S. (1992). *Progr. Colloid and Polymer Sci.*, **90**, 182.
[61] Maissa, P. and Sixou, P. (1989). *Liq. Crystals*, **5**, 1861.
[62] Varichon, L. and Ten Bosch (1993). *Liq. Crystals*, **14**, 1635.
[63] Varichon, L. and Ten Bosch (1994). *J. Chem. Phys.*, **100**, 1708.
[64] Brostow, W. (1990). *Polymer*, **31**, 595.
[65] Brostow, W. and Hess, M. (1992). *Mater. Res. Soc. Symp.*, **225**, 57.
[66] Brostow, W., Dziemianowicz, T. S., Romanski, J. and Weber, W. (1988). *Polymer Eng. and Sci.*, **28**, 785.
[67] Gedde, U. W. and Wiberg, G. (1998). Chapter 10 in Mechanical and Thermophysical Properties of Polymer Liquid Crystals (Brostow, W., Ed.), Chapman & Hall, London.
[68] Photinios, D. J., Samulski, E. T. and Toriumi, J. (1990). *J. Phys. Chem.*, **94**, 4688.
[69] Photinios, D. J., Samulski, E. T. and Toriumi, J. (1990). *J. Phys. Chem.*, **94**, 4694.
[70] Photinios, D. J., Samulski, E. T. and Toriumi, J. (1991). *J. Chem. Phys.*, **95**, 2758.
[71] Photinios, D. J., Samulski, E. T. and Toriumi, J. (1991). *Mol. Cryst. Liq. Cryst.*, **204**, 161.
[72] Rusing, I., Dedier, J., Filliatre, C., Godinho, M. H., Varichon, L. and Sixou, P. (1993). *J. Polymer Sci. Chem.*, **31**, 595.
[73] Sato, T., Sato, Y., Umemura, Y., Teramoto, A., Nagamura, Y., Wagner, J., Weng, D. X., Okamoto, Y., Hatada, K. and Green, M. M. (1993). *Macromolecules*, **17**, 4551.
[74] Rusing, I., Godinho, M. H., Varichon, L., Sixou, P., Dedier, J., Filliatre, C. and Martins, A. F. (1994). *J. Polymer. Sci. Phys.*, **32**, 1907.
[75] Yamacishi, T., Guittard, F., Godinho, M. H., Martins, A. F., Cambon, A. and Sixou, P. (1994). *Polym. Bull.*, **32**, 47.
[76] Yoon, D. Y., Masciocchi, N., Depero, L. E., Viney, C. and Parrish, W. (1990). *Macromolecules*, **23**, 1793.
[77] Brostow, W. and Walasek, J. (1996). *J. Chem. Phys.*, **105**, 4367.
[78] Volkenstein, M. V. (1963). Configurational Statistics of Polymer Chains, Interscience, New York.
[79] Flory, P. J. (1969). Statistical Mechanics of Chain Molecules, Interscience, New York.
[80] Isihara, A. (1971). *Adv. Polymer Sci.*, **7**, 499.
[81] Landau, L. and Lifshitz, E. (1958). Statistical Physics, Addison-Wesley, Reading, MA.
[82] Maier, W. and Saupe, A. (1959). *Z. Naturforsch. A*, **14**, 882.
[83] Maier, W. and Saupe, A. (1960). *Z. Naturforsch. A*, **15**, 287.
[84] Kricheldorf, H. R. and Erxleben, J. (1990). *Polymer*, **31**, 994.
[85] Kricheldorf, H. R., Schwartz, G., Domschke, A. and Linzer, V. (1993). *Macromolecules*, **26**, 5161.

[86] Kricheldorf, H. R., Linzer, V. and Bruhn, Chr. (1994). *J. Macromol. Sci. Chem.*, **31**, 1315.
[87] Kricheldorf, H. R., Linzer, V., de Abajo and de la Campa, J. (1995). *J. Macromol. Sci. Chem.*, **32**, 311.
[88] Kricheldorf, H. R. and Linzer, V. (1995). *Polymer*, **36**, 1893.
[89] Brostow, W., Hibner, K. and Walasek, J. (1999). In preparation for publication.
[90] Sawyer, L. C. and Jaffe, M. (1986). *J. Mater. Sci.*, **21**, 1897.