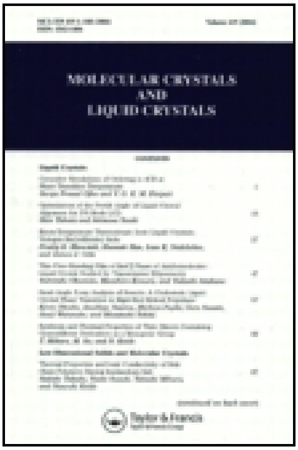

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Critical Points and Re-Entrance in Liquid Crystalline Side-Chain Polymers

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CRITICAL POINTS AND RE-ENTRANCE IN LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS

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Abstract Competing nematic and smectic A phases of comb-like polymers are described by combining Maier-Saupe and McMillan type theories with the worm concept of semi-flexible polymers. There are as few material parameters as possible: main chain flexibility and phenomenological coupling constants. New qualitative predictions, the existence of critical points and re-entrant nematic phases, as well as quantitative predictions for comparison with experiments are provided. A new mechanism for thermotropic nematic biaxiality which is specific of side-chain polymeric liquid crystals is found.

INTRODUCTION

In contrast to isotropic polymers, their liquid crystalline counterparts have been shown to exhibit rather unusual, anisotropic chain configurations /1/. As for nematic main-chain polymers a strong, exponential, temperature dependence of the chain extension has been predicted by de Gennes /2/, who introduced the concept of thermally activated hairpins. A more quantitative theory which includes this effect and also describes the nematic-isotropic transition has been developed by

Warner et al /3/. For smectic A comb-like polymers the concept of layer hopping has been introduced and evaluated quantitatively by Renz and Warner /4/. Quite recently, this idea has received some experimental support from small-angle neutron scattering (SANS) measurements which are, at least, compatible with an exponentially varying coil anisotropy (see Noirez et al., this issue). The aspects of chain configurations are discussed in detail by Warner, this issue.

The large entropy reservoir inherent in polymer flexibility is an essential point which distinguishes polymeric liquid crystals from their low-molecular mass counterparts. In combined side-chain polymers /6/, mesogenic side chains are attached to a semi-flexible, also mesogenic main chain by a flexible spacer which allows for separate ordering tendencies of main and side chains. In order to describe the consequent competition between main and side chain order quantitatively, a mean-field type theory of uniaxial nematic phases has been developed /7/.

In the next section, I am going to present the basic ideas of this theory in order to explain the new features in the phase diagrams (critical points and re-entrant nematic phases) and to discuss connections with experiments. Furthermore I will be showing the extension of the theory to describe smectic A phases. Finally mechanisms to reach biaxial thermotropic nematic phases will be discussed.

UNIAXIAL NEMATIC PHASES (cf. /7/)

Figure 1 shows the three stable nematic phases which are characterized by the sign of the two Maier-Saupe order parameters $S_A = \langle P_2(\cos \vartheta_A)\rangle$ of side chains and $S_B = \langle P_2(\cos \vartheta_B)\rangle$ of main chains.

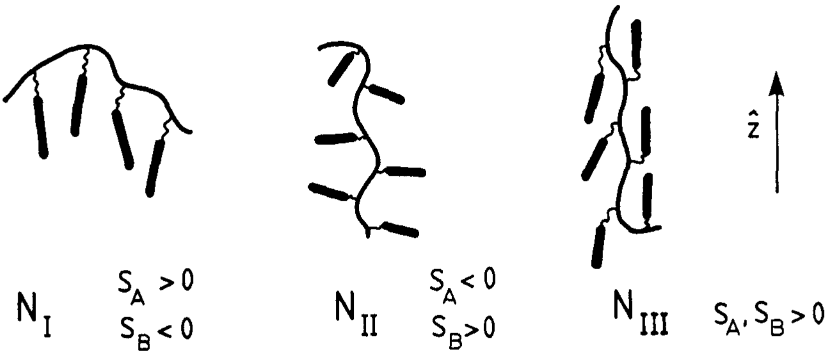

Fig. 1: Chain configurations in uniaxial nematic phases

Phases N_I and N_{III} have been observed using different techniques in melts of Polymethacrylates (SANS /1/, photoelastic /8/, NMR /9/) and in Polyacrylates or Polysiloxanes (SAXS /10/, NMR /9/) respectively. In the case of phase N_{II} the situation is less clear. It could appear in combined polymers. Recently a transition deviding the nematic range into two regions of different nematic phases has been found /5/. Biaxial derivatives of N_{II} might occur, too (see below).

In essence, the theory uses only four material parameters, an effective bending energy $\bar{\epsilon}$

accounting for the main-chain stiffness and three effective nematic coupling constants (as in Maier-Saupe theory) $\bar{v}_A$, $\bar{v}_B$ and $\bar{v}_C$ describing the side-side, main-main and main-side chain coupling respectively. $\bar{v}_C$ contains the competing influence of hinges prefering a perpendicular alignment and of nematic coupling prefering a parallel alignment of main and side chains. All four parameters are effective energies per unit cell (consisting of one side chain, spacer and part of the main chain between two hinges). It seems conceivable to determine these parameters from part of the experimental data in order to obtain predictions for independent experiments without adjustable parameters.

The two self-consistency equations can be evaluated analytically to give

$$\bar{v}_C S_B = k_B T \, g_A^{-1}(S_A) - \bar{v}_A S_A \tag{1}$$

$$\bar{v}_C S_A = (3\bar{\epsilon})^{-1}(k_B T)^2 g_B^{-1}(S_B) - \bar{v}_B S_B \tag{2}$$

where g_A, g_B are universal functions, the Maier-Saupe function and a certain function derived from the lowest eigenvalue of the spheroidal wave equation respectively. A graphical illustration is given in figure 2. Intersections correspond to solutions, whose local stability can be determined from a slope rule. The solution with minimal free energy can be shown to be found from Maxwell-like area rules as indicated in fig. 2.

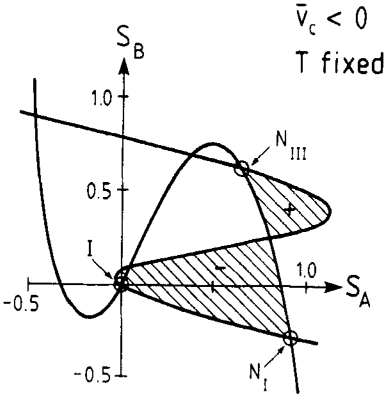

Fig. 2: Order parameter diagram above N_I-N_{III} transition. The difference of the shaded areas represents the difference of free energy between the phases N_I and N_{III}.

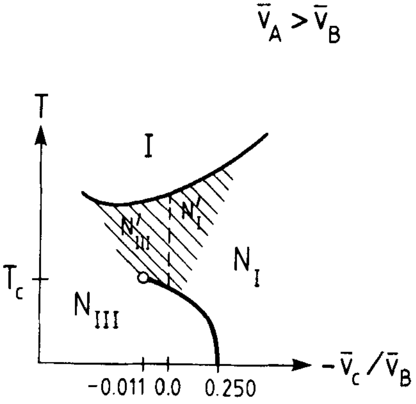

Fig. 3: Phase diagram showing the first order transitions (solid lines) critical point (open circle) and linear response region (shaded).

To be specific, we now consider the phase diagram for comb-polymers with a slightly mesogenic backbone i.e. $\bar{v}_A/\bar{v}_B >> 1$ (Fig. 3). The isotropic-nematic transition is driven by the teeth of the comb: $S_A > 0.4$. The backbone is coupled to the teeth via $\bar{v}_C$ and exhibits a small positive (N'_{III} phase) or negative (N'_I) paranematic response according to the sign of $\bar{v}_C$ which is determined by the competing influence of hinge effect and nematic tendency, as described above. On cooling, the backbone will undergo its paranematic-nematic transition in the internal field $\bar{v}_C S_A$ of the teeth. For $\bar{v}_C > 0$, the field supports the N'_{III}-N_{III} transition. Therefore a critical point occurs if the field reaches a critical magnitude. Assuming nearly complete side chain order at these temperatures, we obtain $(\bar{v}_C/\bar{v}_B)_{crit} \simeq 0.01$ where the precise numerical value is given in /11/. For $\bar{v}_C < 0$, the field acts against the N'_I-N_{III} transition. Finally this transition is completly suppressed and N_I is the only stable phase if $\bar{v}_C/\bar{v}_B < -1/4$. A similar situation with N_{III}/N_{II} phases holds if $\bar{v}_A/\bar{v}_B << 1$.

Experimentally, $\bar{v}_C$ is controlled by the chemical structure, but there is a way of varying $\bar{v}_C$ continuously from its value in a melt: Small amounts of teeth-like low-molecular mass nematics can be solved without problems (swelling). Favorite substances for studying nematic-nematic transitions and reaching the predicted critical point by swelling are combined polymers /6/.

Re-entrant uniaxial nematic phases should occur for $\bar{v}_C < 0$ (Fig. 5). This effect is intimately related to the backbone flexibility and therefore typical of polymeric liquid crystals. Due to the presence of bending energy $\bar{\epsilon}$, different powers of T enter into the prefactors of the universal fcts of eqs. (1) and (2). This leads to a

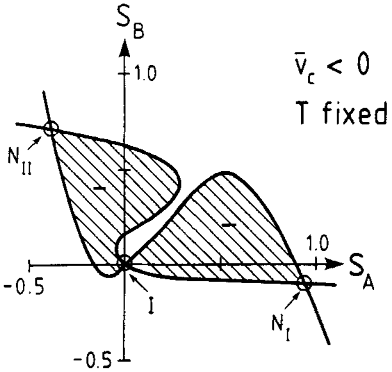

Fig. 4: Order parameter diagram showing the subtle balance of free energy of the phases N_I and N_{II} compared to I.

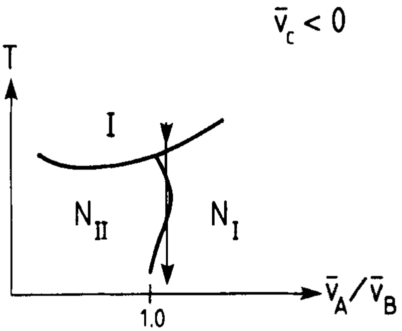

Fig. 5: Phase diagram showing re-entrant nematic phase N_I on cooling (arrow).

subtle balance between the free energies of phases N_I and N_{II} as demonstrated in figure 4. The crucial point in finding re-entrancy experimentally is to modify the spacers in the main-chain in such a way to make the change in backbone flexibility a dominant effect in the accessible nematic temperature range.

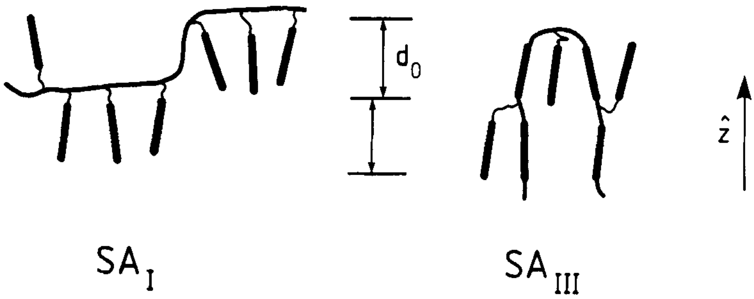

Fig. 6: Chain configurations in uniaxial smectic A phases

UNIAXIAL SMECTIC A PHASES (cf. /4/,/12/)

Figure 6 shows the two stable smectic phases, SA_I derived from N_I with an oblate polymeric coil and SA_{III} derived from N_{III} with a prolate polymeric coil whose shape does not differ drastically in phases N_{III} and SA_{III}. According to McMillan, smectic order parameters have to be introduced to describe the spatial variation and their correlation to the nematic order. The partition function of the smectic backbone is difficult to calculate since, in addition to the orientational restriction, spatial confinement occurs which is not accessible from a standard perturbation theory. Instead, projection methods have to be used to obtain the real space conditional partition function /4,13/. Proceeding this way, rich phase diagrams can be derived which also allow prolate-oblate, oblate-prolate and first or second order nematic-smectic transitions.

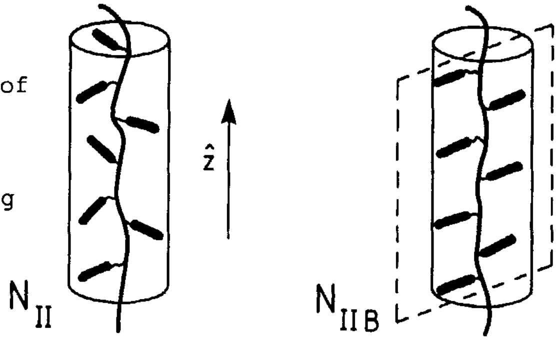

Fig. 7: Formation of biaxial phase N_{IIB} by spontaneous symmetry breaking

BIAXIAL NEMATIC PHASES (cf. /14/)

In low-molecular mass liquid crystals, the existence of biaxial thermotopic nematic phases was predicted a long time ago /15/. For these, a necessary condition is the microscopic biaxiality of the single molecule. Because of the concurrent tendency to form smectics or to even crystallize, such biaxial thermotropic nematics are hardly found /16/. Similar unwanted spatial order is also encountered with biaxial stiff macromolecules (Ballauff, Herrmann-Schönherr et al., this issue).

Unlike the classical mechanism just described, we predict the formation of biaxial thermotropic nematic polymers by spontaneous symmetry breaking for uniaxial brush-like semi-flexible macromolecules (Fig. 7).

Since the side chains contribute less to the free energy in phase N_{II} $(\bar{v}_C < 0)$ than in phase N_{III} $(\bar{v}_C > 0)$ they can be shown to lower their free energy by parallel alignment in a direction perpendicular to the nematic director. Quantitatively this can be derived from a theory which provides for biaxial side chain order via an order parameter $S_{A,2} = \langle \sin^2 \vartheta_A \cos 2\varphi_A \rangle$. The relevant coupling parameter $\bar{v}_{A2} = 3/4\ \bar{v}_A - \bar{v}_t$ controls the transition temperature with $\bar{v}_t$ denoting an effective stiffness constant due to angular correlations of neighbouring teeth.

CONCLUSION

Competition of energy gain by liquid crystalline order and of entropy loss by configurational restrictions on the polymer gives rise to several new phenomena unique for liquid crystalline polymers.

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