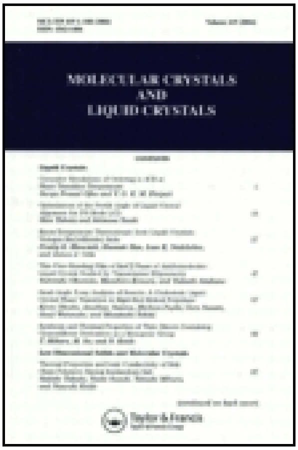

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TRANSITIONS IN NEMATIC NETWORKS

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ABSTRACT Worm and comb-like nematic polymers have their shape influenced by the surrounding nematic environment. Instead of having spherical conformations they are either elongated or flattened spheroids. Linking such chains into networks means that they can be distorted away from their natural shape by the application of stress. Alternatively, as temperature is changed subsequent adjustment of chain shape is resisted by the network to which the chain is linked. The resultant conformation is not the natural one.

We show how the classical theory of polymer networks can be used to work out the decrease in entropy and hence the rise in free-energy that enforced change of chain shape entails. This gives a microscopic understanding to the Landau theories that have been proposed to describe nematic networks.

It is found that, if the network is cross-linked in the para-nematic state, that the nematic-isotropic transition temperature of the network is lowered. Crosslinking in the nematic phase raises the transition temperature above the uncrosslinked value.

INTRODUCTION

It has been well documented[1] that a certain class of polymeric materials exhibit a first-order phase transition from an ordered nematic phase to a disordered isotropic phase as the temperature is raised through some material dependent critical temperature,

T_C. These polymeric materials are invariably constructed from short rigid chemical units that themselves exhibit liquid crystalline properties (i.e. are mesogenic) linked together by semi-flexible, non-mesogenic sections in one of three possible ways indicated diagramatically below:

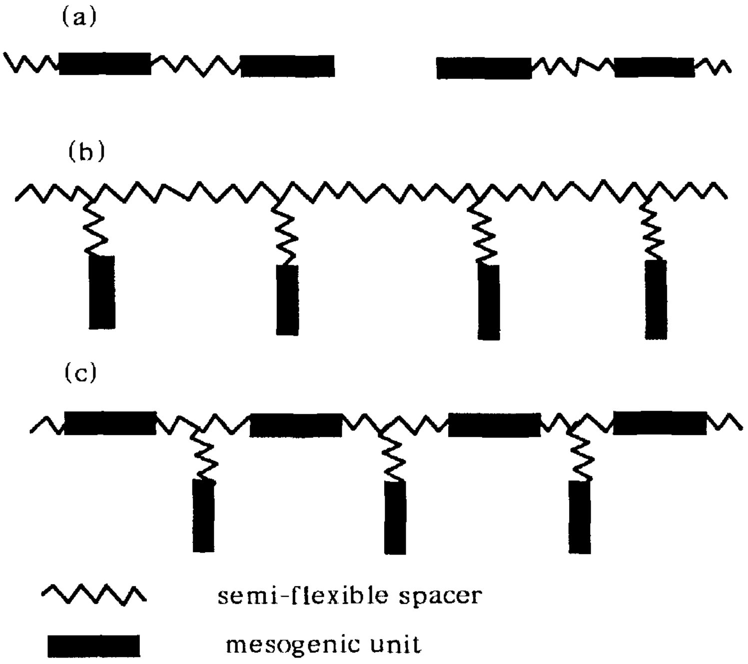

FIGURE 1: Types of nematic polymers

Compounds of type (a) having mesogenic units incorporated entirely within the main polymer sequence, or backbone, are known as worms. Compounds of type (b) and (c) which have side groups attached to the bacbone of the polymer are termed combs.

Just as with ordinary low molecular mass liquid crystals, worms exhibit only one nematic phase. This is because there exists only one order parameter for the molecule, that being the one that represents the mean orientation of backbone elements and it may be either zero or positive, the negative case representing an unstable configuration. The situation for combs is complicated by the fact that there exist two order parameters, S_A, S_B: one each to describe the orientation of the side-chains and backbone respectively. This, in consequence, gives rise to three types of nematic phases characterised by the various possible sign combinations of the two order parameters that are still energetically stable (i.e. $S_A>0, S_B>0$; $S_A>0, S_B<0$; $S_A<0, S_B>0$) - see Warner this issue.

It has been shown[2] that for the nematic phase in which the side chains of a comb align parallel to the ordering field that, because the backbones are coupled to the side-chains, the polymeric backbone is compelled to lie in the plane parallel to the ordering field ($S_A>0, S_B<0$). Consequently, the natural shape for a long molecule possessing some degree of ordering of this type is an oblate spheroid. In a similar fashion in melts, the other two nematic phases of combs and the single nematic phases of worms, result in an overall distortion of the polymer into prolate distributions, in distinction to the spherical shape characteristic of the isotropic phase. Consequently, irrespective of whether or not the material is a worm or a comb, each polymer must undergo a spontaneous deformation from its natural random shape as the temperature is lowered from the isotropic state to a nematic state, due to the nature of a first-order phase transition.

Because it is indeed possible to crosslink melts of these nematic materials to form networks[3], one may ask what effect this will have upon the transition temperature? This question has been answered in part by de Gennes[4] who, employing symmmetry principles, derived a phenomenological model of a Landau theory for systems crosslinked in the nematic state and showed that a rise in the nematic-isotropic transition temperature relative to that of the uncrosslinked sample results. This phenomenological approach has the disadvantage, however, of not providing a microscopic understanding of this phenomenon.

In the remainder of this paper a coupled Maier-Saupe/polymer theory, first appplied by Wang and Warner[5] to studies of the phases of melts of polymeric liquid crystals and herein adapted to crosslinked samples of these melts shall be outlined. Our aim is to gain further insights into the phenomenological studies of de Gennes and to extend these results to crosslinking in isotropic and para-nematic states.

RESUME OF THEORY OF MELTS

In order to appreciate the fundamental model adopted in pursuit of the afore-mentioned goal, it is necessary to outline the work of Wang and Warner. Their model tacitly assumes that the unusual properties of polymeric liquid crystals are a consequence of the competition between the drive to maximise entropy (and hence minimise the free-energy) subject to the orientational order imposed by their liquid crystalline nature. Indeed, it is further assumed that entropy effects are dominant and that internal energy changes due to steric interactions between neighbouring molecules may be neglected apart the role that it has to play in inducing orientational order itself.

Consequently, by determining from first principles an expression for the entropy of a sample of a melt, it is possible to determine the phases of the material. In the full theory, the discrete nature of the backbones of molecules of type (a) and (c) of figure 1 is approximated by assuming that a backbone exhibits the dual properties of flexibility and nematic ordering along its entire length. Assuming this and using a mean field approximation, Wang and Warner recognised that the theory of these materials could be cast in the guise of a spherical wave equation. (For the purposes of this paper, however, it is not relevent to delve into a detailed treatment of the solutions of this equation. This analysis can be found elsewhere.) By this means it was shown that for melts the first-order phase transition of combs can be modelled by a Landau theory where the free-energy is expressed in the following way:

$$F_1(\Lambda) = {}^1/_2A(T-T^*)\Lambda^2 + {}^1/_3B\Lambda^3 + {}^1/_4C\Lambda^4 \qquad (1)$$

with A, B and C constants such that A,C>0, B<0 and can be determined from the full microscopic theory. For the purposes of the current argument, though, it is not necessary to do this as all relevant physical quantities can be determined as simple functions of A, B and C, i.e. the transition temperature is given by:

$$T_C = T^* + {}^2/_9B^2/_{AC} \qquad (2)$$

and the order parameter at the transition by:

$$S^* = -{}^2/_3B/_C \qquad (3)$$

These three equations together provide an acceptable theory of the phase transition of a nematic polymeric material.

EFFECT OF CROSSLINKS

When the melt is crosslinked to form a network, our microscopic theory shows that entropic additions to the free-energy arise[6]. This is because the volume of phase-space occupied by the chain is less when crosslinks are present in the sample than in the melt where all parts of the chain are free to move. Effectively, the decrease gives rise to elastic energy. The way in which these extra terms arise can best be illustrated for the case where the melt is crosslinked in the isotropic phase. Normal distribution theory[7] for polymer systems dictates then that the probability distribution between crosslinks separated by a displacement, $\underline{R}$, is given by:

$$P_o(\underline{R}) \sim \exp(-3\underline{R}^2/2\ell_o L) \qquad (4)$$

where the o subscript indicates the state of formation; L is the length of the chain between crosslinks; and ℓ_o is the effective step-length at the temperature of network formation. It is for this reason that the chain is said to be Gaussian. In the nematic phase this probability distribution becomes:

$$P(\underline{R}) \sim (\ell_o{}^3/\ell_z\ell_p{}^2)^{1/2}\exp(-{}^3/_2\{R_z{}^2/\ell_z L+\underline{R}_p{}^2/\ell_p L\}) \qquad (5)$$

where two effective step-lengths, ℓ_z and ℓ_p, have been introduced, the former parallel and the latter perpendicular to the ordering direction respectively; and $\underline{R}=(R_z,\underline{R}_p)$. The step-lengths couple to the effective order parameter, Λ. This anisotropy of equation (5) has been observed in the nematic phase of some polymeric systems[2].

The free-energy due to elastic effects is the average over the initial distribution P_o of this phase space average i.e.,

$$\Delta F_{el} = -k_B T \langle \ln P \rangle_{P_o} \qquad (6)$$

This represents a rise in the free-energy since $P_o(\underline{R})$ does not reflect the true current distribution of crosslinks, which is a function of Λ and it is as if the network has been strained in order to remain with the initial separation between crosslinks, $\underline{R}$. Performing this average over P_o one obtains:

$$\Delta F_{el} = 1/_2 N_x k_B T(\ell_o/\ell_z + 2\ell_o/\ell_p) + 1/_2 N_x k_B T \ln(\ell_o \ell_p{}^2/\ell_o{}^3) \qquad (7)$$

where N_x is the number density of strands. The assumption so far has been that the chains are long enough compared with their persistence length that they may by described by equations (4) and (5) and, consequently, we are not presenting a theory of gelated stiff rods. Equation (7) is the classic result of network theory modified to the present 'pseudo-Gaussian' case.

It is a well accepted fact that if the degree of order at the microscopic level is altered, a macroscopic deformation of the network will result. To include this effect in the theory, the crosslink points are allowed to deform affinely. Minimising the elastic free-energy with respect to an affine uniaxial strain the corresponding physical, stable free-energy expression can be determined and is given by:

$$\Delta F_{el} = \text{const}.\phi.(W - \ln W) \qquad (8)$$

where

$$W(\Lambda, \Lambda_o) = \{\ell_p{}^2(\Lambda_o)\ell_z(\Lambda_o)/\ell_p{}^2(\Lambda)\ell_z(\Lambda)\}^{1/3} \qquad (9)$$

where Λ_0 refers to the value of the effective order parameter, Λ, upon crosslinking the melt. (Note that ΔF_{el} is proportional to the crosslink density, ϕ). If the free-energy of the melt is included, the total free-energy of the network may be written as:

$$F(\Lambda) = F_1(\Lambda) + \Delta F_{el}(\Lambda) \qquad (10)$$

with F_1 representing the Landau free-energy of equation (1). Again using the molecular model of Wang and Warner, the two length scales, ℓ_p and ℓ_z, can be determined in perturbative fashion up to second order in Λ. Substituting these expansions and equations into the expression for the free-energy, a new transition temperature could be determined via equation (2).

CONCLUSIONS

In essence, the elastic free-energy terms contains only quartic and quadratic additions to the standard Landau theory[6]. These terms arise because the networks have to be strained (thus raising the free-energy) in order to allow the chains to adopt the shape natural to the currently prevailing conditions. The procedure for determining the crosslink transition temperature outlined in the above section yields[6] the result that if the sample is crosslinked when the order parameter is less than $1/\sqrt{2}$ times the uncrosslinked value of the order parameter at the melt transition temperature, the network transition temperature is lowered by an amount proportional to the crosslink density. Otherwise it is raised, again by an amount that is proportional to the crosslink density.

The perturbative expansions for the values of ℓ_z and ℓ_p have only been evaluated to second order in Λ. Higher terms might be required in practice to gain accurate values for the transition temperature since the network undergoes a first-order transition and the order parameter in the nematic phase is not small.

In summary, a molecular theory of worm and comb networks has been constructed and from it the effect of crosslinking upon the transition temperature has been determined. Classical elasticity theory, adapted to take into account the nematic nature of the materials, together with a microscopic treatment of the free-energy of comb and worm chains yield results that are consistent with de Gennes.

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