Theory of smectic ordering in melts of polymers containing mesogenic units

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A theory is constructed for nematic–smectic and smectic *A*–smectic *C* transitions in melts of linear macromolecules with mesogenic units in the main chain. It is shown that the nematic–smectic transition is a first-order transition, while the smectic *A*–smectic *C* transition is a continuous second-order transition.

In the present paper we propose a molecular theory that makes it possible to describe smectic transitions and the structure of smectic phases in a melt of multiblock linear macromolecules containing rigid mesogenic units separated by flexible units (Fig. 1). A similar theory was previously developed for a melt of diblock polymers containing a rigid unit and a flexible unit.[1]

We employ the following model of a macromolecule. The rigid blocks are rods of length L and diameter $d(L/d \gg 1)$. The flexible blocks are modeled by ideal beads on a massless filament. A block contains N beads, each having volume v, and the mean-square distance between neighboring beads is equal to a^2. A chain contains $N^* \gg 1$ rigid blocks. The interaction between blocks is characterized by the Flory parameter χ.[2]

We make one more assumption about the degree of ordering of the rigid units. We assume that in the region of the nematic–smectic transition and in the smectic phase the rigid fragments are packed parallel to one another and orientation fluctuations can be neglected.

The following dimensionless parameters play an important role in the proposed theory:[1]

$$\varphi = \frac{\lambda}{1+\lambda}, \quad \lambda = \frac{Nv}{Ld^2}, \quad \varkappa = \frac{Na^2}{L^2}, \quad \nu = \frac{\varkappa}{\lambda}.$$

The quantity φ is the volume fraction of the flexible component, and the parameter ν is assumed to be much less than unity ($\nu \ll 1$).

1. FREE ENERGY AND SPINODAL OF THE NEMATIC–SMECTIC TRANSITION

In order to investigate the structure and phase transitions in a melt we must choose the parameters characterizing the state of the system and determine the free energy. The most general position of a system in equilibrium corresponds to the case when the concentration of blocks varies periodically along some axis z and the angle between the z-axis and the axis of a rod is equal to θ (Fig. 2). If we have $\theta = 0$, then the melt is in the smectic *A*-phase; if $\theta \neq 0$, then the melt is in the smectic *C*-phase.[3] We now specify the direction of passage along the chain (Fig. 2). In this case we can talk about the starting and final points of a rod. We introduce the distribution functions $\tilde{f}_0(z)$ and $\tilde{f}_1(z)$ of the starting points of rods, which have, respectively, positive and negative projections on the z-axis. It is obvious that the functions $\tilde{f}_0$ and $\tilde{f}_1$ and the angle θ completely characterize the equilibrium state of the system.

In the subsequent analysis it is convenient to take the quantity $L\cos\theta$ as the unit of length and to scale the functions $\tilde{f}_0$ and $\tilde{f}_1$ and the free energy by the area $d^2/\cos\theta$ in the xy plane, perpendicular to the z-axis. Then the volume per unit length remains constant as the angle θ varies.

The volume fraction of rods in a neighborhood of the point z can be written in the form

$$\eta(z) = \int_0^1 \sigma(z-s)\,ds, \tag{1.1}$$

where

$$\sigma(z) = f_0(z) + f_1(z+1),$$

$$f_0(z) = \frac{d^2}{\cos\theta}\tilde{f}_0(z),$$

$$f_1(z) = \frac{d^2}{\cos\theta}\tilde{f}_1(z).$$

If the volume fraction of beads in a neighborhood of the point z is equal to $c(z)$, then the condition of incompressibility has the form

$$c(z) + \eta(z) = 1. \tag{1.2}$$

The average volume fractions are equal to

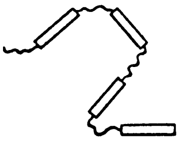

FIG. 1. Model of a macromolecule with mesogenic units in the main chain.

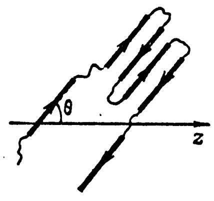

FIG. 2. Chain with a fixed orientation (θ is the angle between the rigid unit and the axis of the translational ordering).

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$$\langle \eta(z)\rangle = 1-\varphi,\quad \langle c(z)\rangle = \varphi,\quad \langle f_i(z)\rangle = \frac{1-\varphi}{2},\quad i=0,1. \tag{1.3}$$

We employ the mean-field approximation to determine the free energy. The range of applicability of the mean-field method is determined from the condition $La^2 < a^3N^{3/2}$.[4] In this case the free energy has three parts (interaction, steric, and conformational):

$$F = F_{int} + F_{ster} + F_{conf}. \tag{1.4}$$

The energy $F_{\rm int}$ corresponds to the effective interaction between blocks of the same type and can be written in the form

$$F_{int} = -T\chi \int \eta^2(z)\,dz, \tag{1.5}$$

where $\chi > 0$ corresponds to attraction and $\chi < 0$ corresponds to repulsion between blocks of the same type.

The steric energy is associated with the fact that the number of possible conformations of the rigid blocks in the melt is limited because the blocks are impenetrable. For $F_{\rm ster}$ we employ the approximate expression[1]

$$F_{ster} = T\int \sigma(z)\ln\frac{1}{1-\eta(z)}\,dz, \tag{1.6}$$

which is asymptotically exact for smectic A and is also applicable if the angle θ is not too close to $\pi/2$.

We now examine the conformational free energy. It cannot be expressed in a closed analytical form in terms of the functions $f_0(z)$ and $f_1(z)$, so that we proceed as follows. In order to calculate the spinodal of the nematic–smectic transition, it is sufficient to know the expansion of the conformational energy in the perturbations $\delta f_i(z)$, for $i=0$ and 1, and $\delta c(z)$ of the uniform state up to terms of quadratic order. This can be done by standard methods.[5,6]

We now consider a system of noninteracting macromolecules and we introduce the weak fields $U(z)$ and $\varphi_i(z)$, $i=0$ and 1, acting on the beads and rods, respectively. In the linear approximation they lead to the following change in the concentrations (in the Fourier representation):

$$\begin{aligned}
-\frac{2T}{1-\varphi}\delta f_0(\alpha) &= NK(\alpha)U(\alpha)B(\alpha)(1+e^{-i\alpha})\\
&\quad +\varphi_0(\alpha)B(\alpha)+\varphi_1(\alpha)e^{-i\alpha-\nu}B(\alpha),\\
-\frac{2T}{1-\varphi}\delta f_1(\alpha) &= NK(\alpha)U(\alpha)B(\alpha)(1+e^{i\alpha})\\
&\quad +\varphi_1(\alpha)B(\alpha)+\varphi_0(\alpha)e^{i\alpha-\nu}B(\alpha),\\
-\frac{T}{N\varphi}\delta c(\alpha) &= S(\alpha)U(\alpha)+\frac{K(\alpha)B(\alpha)}{2N}[\varphi_0(\alpha)(1+e^{i\alpha})\\
&\quad +\varphi_1(\alpha)(1+e^{-i\alpha})].
\end{aligned} \tag{1.7}$$

Here the following notation has been introduced: $a = qL\cos\theta$ is the dimensionless wave vector,

$$y=\frac{\alpha^2\varkappa}{6\cos^2\theta},\quad K(y)=\frac{1-e^{-\nu}}{y},\quad B(y)=\frac{1}{1-e^{-\nu}\cos\alpha},$$

$$S(y)=(2/y)[1-K(y)]+2K^2(y)B(y)\cos\alpha. \tag{1.8}$$

Expressing $U(a)$ and $\varphi_i(a)$ in terms of $\delta f_i(a)$ and $\delta c(a)$ and using the condition of incompressibility, we can write the conformational free energy in the form

$$\begin{aligned}
\delta F_{conf} = \int \{&A_1(\alpha)[\delta f_0(\alpha)\delta f_0(-\alpha)+\delta f_1(\alpha)\delta f_1(-\alpha)]\\
&+A_2(\alpha)\delta f_0(\alpha)\delta f_1(-\alpha)+A_2(-\alpha)\delta f_0(-\alpha)\delta f_1(\alpha)\}\,d\alpha,
\end{aligned} \tag{1.9}$$

where

$$\begin{aligned}
A_1(\alpha) = {}&\frac{1-\varphi}{2\varphi^2}G\frac{\sin^2(\alpha/2)}{(\alpha/2)^2}+\frac{4K^2\cos^2(\alpha/2)G}{(1-\varphi)(1+e^{-\nu})^2}\\
&+\frac{1}{(1-\varphi)B(1-e^{-2\nu})}+\frac{2KG\sin\alpha}{\varphi a(1+e^{-\nu})},
\end{aligned} \tag{1.10}$$

$$\begin{aligned}
A_2(\alpha) = \Big[&\frac{1-\varphi}{2\varphi^2}G\frac{\sin^2(\alpha/2)}{(\alpha/2)^2}+\frac{4K^2\cos^2(\alpha/2)G}{(1-\varphi)(1+e^{-\nu})^2}\\
&+\frac{e^{-\nu}}{(1-\varphi)B(1-e^{-2\nu})}+\frac{2KG\sin\alpha}{\varphi\alpha(1+e^{-\nu})}\Big]e^{i\alpha},
\end{aligned} \tag{1.11}$$

with

$$G(y)=\frac{y}{2}\left[1-\frac{2}{y}\frac{1-e^{-\nu}}{1+e^{-\nu}}\right]^{-1}.$$

The expansion of the total free energy can be written as

$$\delta F = T\sum_{i,j=0}^{1}\int \Omega_{ij}(\alpha)\delta f_i(\alpha)\delta f_j(-\alpha)\,d\alpha \tag{1.12}$$

where

$$\begin{aligned}
\Omega_{00}(\alpha) &= \Omega_{11}(-\alpha)\\
&= A_1+\frac{1}{\varphi}\frac{\sin\alpha}{\alpha}+\left(\frac{1}{2}\frac{1-\varphi}{\varphi^2}-\chi\right)\frac{\sin^2(\alpha/2)}{(\alpha/2)^2},\\
\Omega_{01}(\alpha) &= \Omega_{10}(-\alpha)\\
&= A_2+\left[\frac{1}{\varphi}\frac{\sin\alpha}{\alpha}+\left(\frac{1}{2}\frac{1-\varphi}{\varphi^2}-\chi\right)\frac{\sin^2(\alpha/2)}{(\alpha/2)^2}\right]e^{i\alpha}.
\end{aligned} \tag{1.13}$$

The equation of the spinodal has the form

$$\min_{\alpha,\cos\theta}\det\|\Omega_{ij}\|=0, \tag{1.14}$$

or, after some transformations,

$$\begin{aligned}
\chi=\chi_c = \min_{\alpha,\cos\theta}\frac{1}{2(1-\varphi)}\Big[&\frac{1}{\lambda^2}+\frac{1}{\lambda}\frac{\alpha}{\mathrm{tg}(\alpha/2)}+\frac{(\alpha/2)^2}{\sin^2(\alpha/2)}\\
&\times\frac{1-e^{-\nu}\cos\alpha}{1+e^{-\nu}}+G\Big[\frac{1}{\lambda}+\frac{(1-e^{-\nu})\alpha}{y(1+e^{-\nu})\mathrm{tg}(\alpha/2)}\Big]^2\Big].
\end{aligned} \tag{1.15}$$

Minimization gives the following results. For $\lambda \ll 1$, i.e., if the rigid component predominates, the system is unstable with respect to the formation of a smectic A structure at

$$\chi_{c1} = -\frac{1}{2\lambda^2}(1+\lambda)+\pi^2\left(\frac{5}{6}+\frac{\nu}{6\lambda}\right) \tag{1.16}$$

with modulation period (in units of L)

$$P=1+\lambda-\pi^2\lambda^3/3. \qquad (1.17)$$

It is evident from the formula (1.16) that the transition into smectic A for $\lambda \ll 1$ occurs for values of the parameter $\chi < 0$, which corresponds to effective repulsion of blocks of the same type. This behavior is caused by the strong steric interaction of the rigid units, which itself enhances the tendency for a layered structure to form.

In the opposite limiting case, $\lambda \gg 1$, the instability arises with respect to smectic C $(\theta \sim \pi/2)$ at

$$\chi_{c2} \approx \lambda/2 \qquad (1.18)$$

with modulation period

$$P_2 \approx \pi \nu^{1/2} L/3^{1/2}. \qquad (1.19)$$

In order to investigate the type of phase transition on the basis of the above approach it is necessary to know the expansion of the free energy up to terms of fourth order in δf_i, $i = 0,1$. This is not the best approach in this case. We use different methods below to examine the question of the type of transition. The answer is that the transition is first-order.

2. STRUCTURE OF THE SMECTIC PHASE FOR $\lambda \ll 1$

We now study in greater detail the structure of the smectic phases. We consider the case when the rigid blocks fill most of the volume of the system ($\lambda \ll 1$). It is easy to verify that when in smectic A the rigid and flexible units are completely separated the period of the structure will be equal to exactly $P = 1 + \lambda$, and in the case when the rigid and flexible units are not completely separated the period will be close to this value. We investigate the stability of the uniform state of the system with respect to the formation of a smectic structure with period $P = 1 + \lambda + \varepsilon$, where $\varepsilon \ll \lambda$. We assume that the distribution functions of the ends $f_i(x)$, $i = 0, 1$, vary slowly in space. This latter condition-that the gradients are small-makes it possible to obtain an analytical expression for the conformational free energy.

The conformational energy can be calculated by the Lifshitz method.[7,8] Let the distribution functions of the ends $f_i(x)$ and the volume concentration of beads $c(z)$, which can be expressed in terms of $f_i(x)$ via the incompressibility condition (1.2), be given. The conformation of a flexible unit in the smectic phase is, in general, not Gaussian. This latter circumstance can be taken into account by introducing a field $U(z)$ which acts on the beads and changes the conformation of the chain so that the condition of compressibility is satisfied. On the basis of the foregoing facts, the general expression for the conformational energy can be written in the form

$$F_{conf}=-T\sum_{i=0}^{1}\int dx\, f_i(x)\ln\left[\frac{1}{2\psi_i(x)}\sum_{j=0}^{1}\int G_j(y,x|U)\psi_j(y)dy\right]$$
$$-T\frac{N}{\lambda}\int c(z)U(z)dz. \qquad (2.1)$$

The transition probability function is equal to

$$G_j(y,x|U)=\int g[y+(-1)^j-z_1]\exp[-U(z_1)]g(z_1-z_2)$$
$$\times\exp[-U(z_2)]\ldots g(z_N-x)dz_1\ldots dz_N,$$

$$g(z_i-z_{i+1})=\left(\frac{3N}{2\pi\varkappa'}\right)^{1/2}\exp\left[-\frac{3N}{2\varkappa'}(z_i-z_{i+1})^2\right],$$

$$\varkappa'=\frac{\varkappa}{\cos^2\theta}. \qquad (2.2)$$

The distribution functions $f_i(x)$, $i = 0, 1$, are expressed in terms of the functions $\psi_i(x)$, $i = 0, 1$, as follows:

$$f_0(x)=\frac{1}{2}\psi_0^+(x)\sum_{j=0}^{1}\int G_j(y,x|U)\psi_j(y)dy,$$
$$f_1(x)=\frac{1}{2}\psi_1^+(x)\sum_{j=0}^{1}\int G_j(y,x|U)\psi_j(y)dy, \qquad (2.3)$$

where $\psi_0^+(x) = \psi_1(x+1)$ and $\psi_1^+(x) = \psi_0(x-1)$.

The formulas (2.3) can be simplified by expanding $U(x)$ and $\psi_i(x)$ in terms of the gradients and using the condition of periodicity:

$$f_0(x)=\frac{1}{2}\psi_1(x-\lambda)\Big\{\psi_0(x+\lambda)+\psi_1(x-\lambda)$$
$$+\frac{\varkappa'}{6}\frac{\partial^2}{\partial x^2}[\psi_0(x+\lambda)+\psi_1(x-\lambda)]$$
$$-\frac{\varkappa'}{6}N\frac{\partial U}{\partial x}\frac{\partial}{\partial x}[\psi_0(x+\lambda)+\psi_1(x-\lambda)]$$
$$-\frac{\varkappa'}{12}N\frac{\partial^2 U}{\partial x^2}[\psi_0(x+\lambda)+\psi_1(x-\lambda)]$$
$$+\frac{\varkappa'}{18}\left(N\frac{\partial U}{\partial x}\right)^2[\psi_0(x+\lambda)+\psi_1(x-\lambda)]\Big\}e^{-NU},$$
$$f_1(x)=\frac{1}{2}\psi_0(x+\lambda)\Big\{\psi_0(x+\lambda)+\psi_1(x-\lambda)$$
$$+\frac{\varkappa'}{6}\frac{\partial^2}{\partial x^2}[\psi_0(x+\lambda)+\psi_1(x-\lambda)]$$
$$-\frac{\varkappa'}{6}N\frac{\partial U}{\partial x}\frac{\partial}{\partial x}[\psi_0(x+\lambda)+\psi_1(x-\lambda)]$$
$$-\frac{\varkappa'}{12}N\frac{\partial^2 U}{\partial x^2}[\psi_0(x+\lambda)+\psi_1(x-\lambda)]$$
$$+\frac{\varkappa'}{18}\left(N\frac{\partial U}{\partial x}\right)^2[\psi_0(x+\lambda)+\psi_1(x-\lambda)]\Big\}e^{-NU}. \qquad (2.4)$$

The volume fraction of beads $c(z)$ can be written in the form of an expansion:

$$c(z)=\lambda\Big\{f_0(z)+f_1(z)+\frac{\lambda}{2}[f_0'(z)-f_1'(z)]$$
$$+\frac{\lambda^2}{6}[f_0''(z)+f_1''(z)]\Big\}. \qquad (2.5)$$

It will be convenient to employ below as the independent variables the distribution function of the ends

$$\sigma(z)=f_0(z)+f_1(z)+\lambda f_1'(z)-{}^1/_2\lambda^2 f_1''(z)$$

and the function

$$\rho(z)=f_0(z)-f_1(z).$$

It is easy to obtain an equation for the potential $U(z)$

from the condition of incompressibility and using the notation introduced above:

$$\frac{\varkappa'}{18}\sigma(x)\frac{\partial U}{\partial x}=\lambda\rho(x)+\frac{\lambda^2}{3}\frac{\partial\sigma(x)}{\partial x}+\frac{2\varepsilon}{\lambda}\left(\sigma-\frac{1}{1+\lambda}\right). \tag{2.6}$$

On the basis of what we have said above and after expanding the free energy (2.1) the final expression for the conformational free energy can be written in the variables σ and ρ in the form

$$F_{conf}=T\int\left\{-\frac{3}{2}\left(1+3\frac{\lambda}{\nu}\right)\frac{\rho(x)}{\sigma(x)}(\rho-\lambda\sigma')+\left(\frac{\varkappa'}{24}-\frac{\lambda^2}{4}\right)\frac{\sigma'^2}{\sigma}+\frac{\lambda^4}{8\sigma\varkappa'}\left[\sigma'-\frac{12\varepsilon}{\lambda^3}\int_{-\infty}^{x}\left(\sigma(x')-\frac{1}{1+\lambda}\right)dx'\right]^2\right\}dx. \tag{2.7}$$

The expansions for the interaction and steric parts of the free energy were obtained in Ref. 1:

$$F_{int}=-T\chi\lambda^2\int\sigma^2(z)\,dz,$$

$$F_{ster}=T\int\left[\sigma(z)\ln\frac{1}{\lambda\sigma(z)}+\frac{\lambda^2}{8}\frac{\sigma'^2}{\sigma}\right]dz. \tag{2.8}$$

Combining the expressions (2.7) and (2.8) and minimizing with respect to ρ the resulting sum, we obtain the final expression for the free energy as a function of $\sigma(x)$:

$$F=T\int\left\{-\sigma(x)\ln[\lambda\sigma(x)]+\left(\frac{\varkappa}{24}+\frac{\lambda^2}{4}\right)\frac{\sigma'^2(x)}{\sigma(x)}-\chi\lambda^2\sigma^2\left(1-\frac{\lambda^2\sigma'^2}{12\sigma^2}\right)+\frac{\lambda^4}{8\sigma\varkappa}\left[\sigma'-\frac{12\varepsilon}{\lambda^3}\int_{-\infty}^{x}\left(\sigma(x')-\frac{1}{1+\lambda}\right)dx'\right]^2\right\}dx. \tag{2.9}$$

In order to determine the critical point of the nematic–smectic transition, χ^*_{c1}, and the structure of the smectic, the free energy (2.9) must be minimized with respect to $\sigma(x)$ under the additional condition

$$\int_z^{z+P}\sigma(x)\,dx=1. \tag{2.10}$$

Analysis shows that the most favorable formation is a periodic structure with period $P=1+\lambda$ (Fig. 3). The free energy has the form

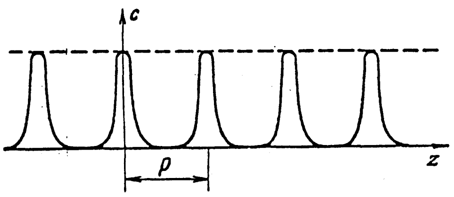

FIG. 3. Profile of the concentration of flexible units in the smectic for $\lambda\ll 1$; $P=1+\lambda$ is the period of the structure.

$$F=T\int\left[-\sigma(x)\ln[\lambda\sigma(x)]+Q\frac{(\sigma')^2}{\sigma}-\tilde{\chi}\sigma^2\right]dx, \tag{2.11}$$

where

$$\tilde{\chi}=\chi\lambda^2,\qquad Q=\frac{\varkappa}{24\cos^2\theta}+\frac{\lambda^2}{4}+\frac{\lambda^4\cos^2\theta}{8\varkappa}.$$

In order to minimize the free energy we make the substitution $\sigma=\tau^{1/2}$. As a result we obtain two branches of the inverse function $z=z(\tau)$ on a period:

$$\pm\frac{z}{4Q^{1/2}}=\int_0^{\tau}\frac{du}{u[\tilde{\chi}\tau_m^2(1-u^2)-\ln u^2]^{1/2}}. \tag{2.12}$$

The maximum value τ_m of the function $\tau(z)$ is determined form the condition

$$\frac{1}{4Q^{1/2}\tau_m^2}=\int_0^1\frac{u\,du}{[\tilde{\chi}\tau_m^2(1-u^2)-\ln u^2]^{1/2}}. \tag{2.13}$$

The difference between the free energies of the inhomogeneous and homogeneous states per period is equal to

$$F(\sigma)-F(\bar{\sigma})=-\ln\tau_m^2-\tilde{\chi}(\tau_m^2-1)+4Q^{1/2}\tau_m^2\times\int_0^1 du[\tilde{\chi}\tau_m^2(1-u)-\ln u]^{1/2}-2\tilde{\chi}\lambda+\lambda\leqslant 0. \tag{2.14}$$

Minimizing the free energy (2.14) with respect to $\cos\theta$ we find that the transition into the smectic structure is a first-order transition and occurs at

$$\chi_{c1}^*\approx-1/\lambda^2, \tag{2.15}$$

and in addition for $\lambda<\nu 3^{1/2}$ the smectic A phase is stabilized while for $\nu/3^{1/2}<\lambda$ the smectic C phase is stabilized. The slope angle in the smectic C phase at the point of the transition is equal to

$$\cos\theta=(\nu/3^{1/2}\lambda)^{1/2}, \tag{2.16}$$

and $\tau_m\sim 1$.

For $\chi=0$ the profile of the bead density in the flexible domain has the form

$$c(z)=\frac{\lambda}{2(\pi Q)^{1/2}}\exp\left(-\frac{z^2}{4Q}\right). \tag{2.17}$$

An increase in χ in the region $\chi>\chi_c$ does not significantly affect the concentration profile of the flexible component up to values $\chi\sim\chi_c^*\sim 1/\lambda$, for which the contribution of the interaction part of the free energy becomes of the same order of magnitude as that of the steric part. For $\chi\gg\chi_c^*$ the smectic structure is completely determined by the interaction and conformational parts of the free energy.

In the nematic phase the ends of the chain are uniformly distributed in space, while in the smectic phase with $\chi>\chi^*_{c1}$ they start to localize in space. As a result of this localization a flexible tie can have straight and loop conformations (Fig. 4) with different energies of stretching. It is obvious that the energy of the straight chain is higher than the energy of the loop chain, and in addition the difference between these energies increases as the ends become more localized, i.e., as χ increases. Thus the fraction of folds in the macromolecule increases with increasing χ.

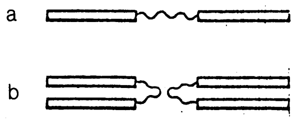

FIG. 4. Conformation of flexible units in the smectic phase: a) straight chain; b) loop chain.

3. STRUCTURE OF THE SMECTIC PHASE FOR $\lambda \gg 1$

We now study the nematic–smectic transition in the case when the flexible component is the dominant component in the volume ($\lambda \gg 1$). As analysis shows, the homogeneous phase is unstable with respect to the formation of a structure consisting of alternating rigid (Fig. 2) and flexible domains. The rigid blocks form domains of thickness 1 (in the scale $L\cos\theta$) and the interval between the domains is equal to S, so that the period of the structure is $P = 1 + S$. The maximum density of the rigid component in the domain is $\eta_{\max} = (1+S)/\lambda$ (Ref. 1). We assume $S \ll \lambda$.

For $\lambda \gg 1$ the interaction and conformation parts of the free energy play the dominant role in the formation of the smectic structure, while the contribution of steric interactions will be small. Assuming narrow domain walls, the conformational free energy can be represented as a sum of three terms:

$$F_{conf} = F_1 + F_2 + F_3. \tag{3.1}$$

The first term is the ideal gas contribution, which is related with the localization of the ends of the rods in a small region $\Delta \ll \varkappa$:

$$F_1 = T \int \left[f_0(z) \ln \frac{2f_0(z)}{1-\varphi} + f_1(z) \ln \frac{2f_1(z)}{1-\varphi} \right] dz. \tag{3.2}$$

The second term results from the presence of the gradient of the bead concentration in the region of the domain wall, and for $\Delta \gg a$ it can be written in the form

$$F_2 = T \frac{\varkappa}{24\lambda \cos\theta} \int \frac{(d\eta/dz)^2}{1-\eta(z)} dz. \tag{3.3}$$

The energy F_3 is the energy of stretching of the flexible units. The configurations of a flexible chain which are shown in Fig. 6 should make the main contribution to F_3. It is obvious that the contribution of the first configuration (straight chain) to the stretching energy per unit length is equal to

$$F_{31} \approx 3S^2 \cos^2\theta / 2\varkappa\lambda.$$

For $S \gg 1$ the stretching energy in the second and third configurations (loop chains) is approximately the same, $F_{32} \sim F_{33}$. We employ the standard method to calculate this energy.[9] The stretching of loop chains is governed by the difference between the distribution functions $f_0(z)$ and $f_1(z)$ of the ends of the chains and the distribution $c(z)/N$ of their centers of mass. Calculations lead to the following result for the stretching energy:

$$F = T \frac{18\lambda}{\varkappa} \int \frac{D^2(z)}{c(z)} dz,$$

$$\operatorname{div} D(z) = f_0(z) + f_1(z) - c(z)/\lambda. \tag{3.4}$$

The energies F_{32} and F_{33} per unit length can be estimated using the formula (3.4):

$$F_{32} \approx F_{33} = 3S^2 \cos^2\theta / 2\varkappa\lambda.$$

It is easy to see that for $S \gg 1$ we have $F_{32} \approx F_{31}$.

We now determine the energy of a domain wall. The attraction energy between blocks of the same type and the energy F_2 make the main contribution to the domain-wall energy. For our structure (see Fig. 5) the domain-wall energy per unit length is equal to

$$F_2 = \frac{\pi}{4} T \frac{1+S}{\lambda^2} \left(\frac{\nu\chi}{6} \right)^{1/2} \frac{1}{\cos\theta}. \tag{3.5}$$

The energy of attraction per unit length is

$$F_{at} = -T\chi(1+S)/\lambda^2, \tag{3.6}$$

and the ideal-gas term is

$$F_1 = T\lambda^{-1} \ln [S(6\chi/\nu)^{1/2}]. \tag{3.7}$$

The total free energy consists of the energy of attraction, the domain-wall energy, the energy of stretching of flexible units, and the ideal-gas term. In order to find the critical value of the parameter χ, for which the smectic structure becomes advantageous (see Fig. 5), and the period of this structure, we minimize the total free energy with respect to S. The calculations show that the transition into the smectic C phase occurs at $\chi^*_{c2} \sim \lambda^{1/3}$. For $\chi > \chi^*_{c2}$ the slope angle in smectic C and the period of the structure are equal to, respectively,

$$\cos\theta = \frac{\pi}{2} \left(\frac{\nu}{3\chi} \right)^{1/2}, \quad P = \frac{2L}{\pi} \chi \left(\frac{\nu\chi}{6} \right)^{1/2}. \tag{3.8}$$

It is obvious from Eq. (3.8) that as χ increases the slope angle of the rigid units in the smectic increases and the period of the structure increases. At the same time, the flexible component is expelled from the region of the rigid domain. When χ reaches the value $\chi \sim \lambda^{1/2}$, complete separation of the rigid and flexible units occurs and the formulas (3.8) are no longer valid. Thus the calculations performed above and the formulas are valid in the region $\lambda^{1/3} < \chi < \lambda^{1/2}$.

4. NARROW-DOMAIN-WALL APPROXIMATION

We now investigate the smectic phase with complete separation of the rigid and flexible units. In this case the period of the structure is equal to exactly $P = L(1+\lambda)\cos\theta$.

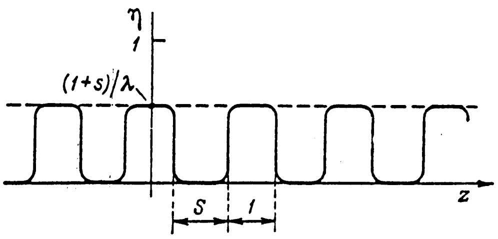

FIG. 5. Profile of the concentration of rigid units in the smectic with $\lambda \gg 1$; $P = 1 + S$ is the period of the structure.

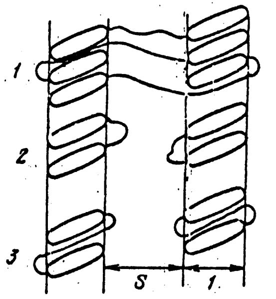

FIG. 6. Conformations of a flexible chain which make the main contribution to the stretching energy.

We begin by determining the structure of the flexible domain. In the flexible domain the chains can be divided into two groups-loop and straight chains (Fig. 7). It is obvious that if the slope angle of the rigid units in the smectic is not very large and $\lambda > \nu$, the chains should be strongly stretched, so that their stretching energy can be found by the method proposed by Semenov.[9] The energy per unit area $d^2/\cos\theta$ of one flexible domain has the form

$$F=\frac{3T}{a^2}p\int_0^R E_1(x)dx+\frac{3T}{a^2}(1-p)\int_0^R d\xi f(\xi)$$
$$\times\int_0^\xi E_2(x,\xi)dx+Tp\ln p+T(1-p)\ln(1-p), \qquad (4.1)$$

where p is the probability that the chain is a straight chain, R is the distance from the domain wall to the center of the domain, $E_1(x)$ is the tension of a straight chain at the point x, $f(\xi)$ is the distribution function of the point of a loop chain farthest from the wall (point of return), and $E_2(x,\xi)$ is the tension at the point x of a loop chain such that the coordinate of the point of return is ξ. In order to minimize the free energy (4.1) it is necessary to take into account the additional conditions that the number of beads in a chain is fixed and the density of the flexible domain is constant:

$$\int_0^R\frac{dx}{E_1(x)}=\frac{N}{2},\quad \int_0^\xi\frac{dx}{E_2(x,\xi)}=\frac{N}{2},$$
$$\frac{p}{E_1(x)}+(1-p)\int_x^R\frac{dx}{E_2(x,\xi)}=v^{-1}. \qquad (4.2)$$

Minimizing the energy (4.1) under the additional conditions (4.2) for a fixed fraction p of straight chains leads to the following results. Loop chains are expelled from the center of the domain by the straight chains, since the position of the points of return is limited to the region $\xi\leqslant R^*$ (see Fig. 7). The free energy as a function of the fraction of straight chains p is equal to

$$F(p)=\frac{\pi^2T}{8}\frac{\lambda^2\cos^2\theta}{\varkappa}\left[\left(\frac{R^*}{R}\right)^3\right.$$
$$\left.+\frac{12p^2}{\pi^2}\right]+Tp\ln p+T(1-p)\ln(1-p), \qquad (4.3)$$

where the ratio R^*/R is related to p by the following relation:

$$\operatorname{tg}\frac{\pi(R-R^*)}{2pR}=\frac{\pi R^*}{2pR}. \qquad (4.4)$$

Minimizing the free energy (4.3) with respect to p gives the fraction of straight chains

$$p^*\sim\left(\frac{\varkappa}{\lambda^2\cos^2\theta}\right)^{1/3}\ll 1. \qquad (4.5)$$

In the case $\lambda\ll\nu$ we have $p^*\sim 1/2$.

Thus the most advantageous chain conformation in the region $\lambda\gg\nu$ is the "folded" conformation (Fig. 8). The mean-square distance between the ends of a macromolecule, consisting of $N^*\gg 1$ blocks in the plane of the layer ($R_\perp$) and along the z-axis ($R_\parallel$), is equal to

$$R_\perp^2\approx{}^2/_3a^2NN^*,\quad R_\parallel^2\approx[L(1+\lambda)\cos\theta]^2N^*p^*. \qquad (4.6)$$

In order to determine the period of the smectic structure and the slope angle of the rigid units, in addition to the stretching energy of the flexible chains it is necessary to know the surface tension of the domain walls. This last problem was solved in Ref. 1. The total free energy per period is equal to

$$F=T\frac{\pi^2}{8}\frac{\lambda^2\cos^2\theta}{\varkappa}+T\left(\frac{\varkappa\chi}{3\lambda}\right)^{1/2}\frac{1}{\cos\theta}. \qquad (4.7)$$

It follows from Eq. (4.7) that the dependence of the slope angle of the rods in smectic C on χ has the form

$$\cos\theta=\left(\frac{16}{3\pi^4}\right)^{1/6}\left(\frac{\nu^3\chi}{\lambda^2}\right)^{1/6}, \qquad (4.8)$$

and the period is $P=L(1+\lambda)\cos\theta$. If $\chi=\chi_1=\frac{3}{16}\pi^4\lambda^2/\nu^3$, then a smectic C–smectic A second-

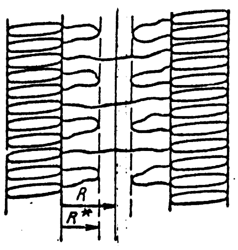

FIG. 7. Distribution of straight and loop chains in the flexible domain when the flexible and rigid blocks are completely separated.

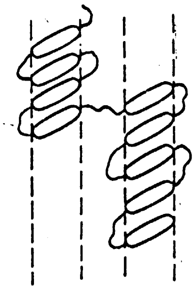

FIG. 8. Folded structure of a macromolecule.

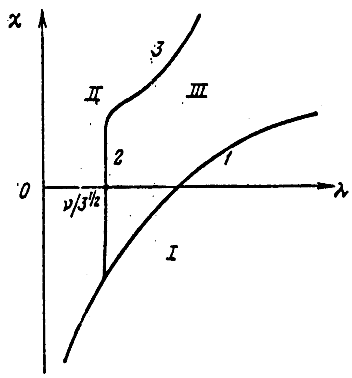

FIG. 9. Phase diagram of the melt in the variables (x,λ). I—nematic phase; II and III—smectic A and C phases.

order transition occurs, so that for $\chi < \chi_1$ the smectic C is stable and for $\chi > \chi_1$ the smectic A is stable.

The results obtained in this paper permit constructing a phase diagram of the states of an anisotropic melt of multiblock linear macromolecules in the variables χ and λ with a fixed geometry of the blocks ($\nu = \text{const}$) (Fig. 9). The region I is the region of existence of the nematic phase, separated from the smectic by the curve *1* with the asymptotes $\chi \sim -1/\lambda^2$ for $\lambda \ll 1$ and $\chi \sim \chi^{1/3}$ for $\lambda \gg 1$; region II is the region of existence of smectic A; and, region III is the region of existence of smectic C. The boundary between smectics A and C passes along the curves *2* and *3*, which are described by the equations $\lambda = \nu/3^{1/2}$ and $\chi \sim \lambda^2/\nu^3$, respectively. The transition to the curve *1* is a first-order transition and the transitions to the curves *2* and *3* are second-order transitions.

Thus our calculations show that the steric interaction significantly affects the stability of the nematic phase in the case when the rigid component predominates in the system. As the length of the flexible units decreases (the fraction of the rigid component increases) the transition into the smectic phase will occur at lower values of χ. Since the parameter χ is inversely proportional to the temperature, the transition into the smectic phase of polymers with shorter flexible units will occur at a higher temperature; this agrees qualitatively with experiment.

Our analysis also shows that the most advantageous conformation of the chain is a folded structure. This is indicated also by the experiment described in Ref. 10.

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