Physics

LIQUID CRYSTALLINE PHASE OF THE DOUBLE-STRAND DNA IN THE POLYMER MATRIX

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The liquid crystalline phase formation by short DNA fragments within the flexible polymer water containing matrix as well as the influence of interaction parameters and volume fraction of polymer on the orientational ordering have been investigated. It has been shown that liquid crystalline order formation in ds-DNA, immeresed in the polymeric matrix occurs with increase of the volume fraction. The volume fraction of transition between isotropic and nematic phases depends on value of the temperature dependendt Flory–Huggins parameter. The obtained results show the effect of the polymer matrix on the ordering in DNA molecules.

Keywords: DNA, polymer, isotropic and nematic phases, DNA ordering.

Introduction. The orientational ordering of the semiflexible and rod-like polymers are of interest because of their important technological applications in high modulus fibers, nonlinear optics and electro-optical devices [1, 2]. Short double-stranded DNA (ds-DNA) with the countrour length of L_r comparable to the persistence length $\tilde{\ell}$ ($\tilde{\ell}$ is estimated as $50 nm$ or 150 baze pairs), which can be approximated as a rigid rod and may serve as a theoretical model to consider the effect of interaction parameters and volume fraction of polymer on the orientational ordering.

In this work phase behavior of short ds-DNA molecules, containing water and multivalent cations, promoting short polymer fragments condensation [3] has been treated. Obtained results showed that the ordered phase formation of ds-DNA was governed by volyme fraction of polymer and temperature.

Results and Discussion. Let us consider a mixture of N_r number of ds-DNAs, schematically described as rods of length L_r and diameter d, and N_p number of flexible polymer molecules with contour length of n_p.

The free energy of mixing for the two types of molecules having both excluded volume interactions and orientation-dependent attractive interactions may be written on the basis of the Onsager theory [4] as:

$$\Delta F_{mix} = F(N_p, N_r) - F_p(N_p) - F_r(N_r), \tag{1}$$

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where $F(N_p, N_r)$ is the free energy of the blend of the two types of molecules, $F_p(N_p)$ and $F_r(N_r)$ are the free energies of the pure polymer and pure ds-DNAs in isotropic phase respectively. The free energy of the rigid rods and flexible polymer mixtures has been estimated in [5] as

$$F(N_p, N_r) = N_p \mu_p^0 + N_r \mu_r^0 + k_B T \left(N_p \ln \frac{c_p}{e} + N_r \ln \frac{c_r}{e} \right) +$$
$$+ k_B T (v_{pp} N_p c_p + 2 v_{rp} N_p c_r) + k_B T \left(v_{rr} \rho N_r c_r - \frac{v_{rr}^2}{2} \chi_{rr} S^2 N_r c_r + N_r \sigma \right), \tag{2}$$

where μ_i^0 $(i = p, r)$ represents the standard chemical potential of the i-type molecule, T is the absolute temperature, $c_i = N_i / V$, is i-type molecule of the concentration, V is the system volume, v_{ij} is the average excluded volume of a pair of i- and j-types of molecules with random orientation and $v_r \approx d^2 L_r$ is the volume of each ds-DNA, χ_{rr} is the rod-to-rod interaction Maier–Saupe parameter [4]. It is assumed that the each ds-DNA rod has a well defined long axis with polar angles θ and φ with the nematic director n. To specify the preferable orientation of the ds-DNA rods, a distribution function $f(\theta, \varphi)$ and the orientational entropy per one ds-DNA rod $\sigma = \int d\Omega f(\theta, \varphi) \ln(4\pi f(\theta, \varphi))$ [6] are introduced. The term describing two ds-DNA rods interaction is written as

$$\rho = \iint d\Omega d\Omega' f(\theta, \varphi) f(\theta', \varphi') |\sin \gamma(\theta, \theta')|, \tag{4}$$

where $\gamma(\theta, \theta')$ is the angle between two ds-DNA rods. The alignment of a ds-DNA rod to the nematic phase director is measured by the order parameter

$$S = \int d\Omega f(\theta, \varphi) P_2(\cos(\theta)), \tag{5}$$

where $P_2(x)$ is the second order Legendre polynomial [7]. Thus, the free energy of mixture becomes a functional of the distribution function $f(\theta, \varphi)$. The distribution function $f(\theta, \varphi)$ is determined by minimizing the free energy (see Eq. (2)) with respect to this distribution function with the normalization condition $\int d\Omega f(\theta, \varphi) = 1$.

For the liquid crystal molecules the Maier–Saupe parameter is supposed to be $\chi_{rr} \cong U_a / k_B T$. The energy U_a can be assigned to the attraction energy of the two parallel ds-DNAs. Taking into account above mentioned conditions the free energy of ds-DNA polymer mixing is transformed to:

$$\frac{\Delta F_{mix}}{N k_B T} = \frac{\phi_p}{n_p} \ln \phi_p + \frac{\phi_r}{n_r} \ln \phi_r + \chi \phi_p \phi_r + \frac{1}{2} (\chi_a + 5/4) \phi_r^2 S^2 - \frac{\phi_r}{n_r} \ln \frac{I_0(\Gamma_0 \phi_r S)}{2}, \tag{6}$$

where $N = V / a^3$ is the total number of the lattice sites, a is the lattice step,

$\chi_a = \pi d^3 \chi_{rr} / 4$, $n_r = L_r / d$ and $\chi = a^3 \left(\frac{2 v_{pr}}{v_p v_r} - \frac{v_{pp}}{v_p^2} - \frac{v_{rr}}{v_r^2} \right)$ is the Flory–Huggins

interaction parameter [7].

The chemical potentials in the nematic phase are given by $\dfrac{\Delta\mu_p(\phi_p, S)}{k_B T} = \dfrac{\partial\Delta F_{mix}}{k_B T \partial N_p}$ for the flexible polymer, and $\dfrac{\Delta\mu_r(\phi_p, S)}{k_B T} = \dfrac{\partial\Delta F_{mix}}{k_B T \partial N_r}$ for the ds-DNA rods. In the isotropic phase the chemical potentials are given by $\Delta\mu_r(\phi_p, 0)$ and $\Delta\mu_p(\phi_p, 0)$ respectively. The attraction between ds-DNA rods is characterised by dimensionless parameter $\chi_a = \dfrac{U_a}{k_B T}$, where U_a shows the orientation dependent attractive (Maier–Saupe) interaction between rods. The phase transition between the isotropic and nematic phases take place, if the chemical potentials $\Delta\mu_r(\phi_p, S)$ and $\Delta\mu_p(\phi_p, S)$ are equal each other. Thus, according to [4, 5], the value of the parameter $\Gamma_0 = \dfrac{L_r}{d}\left(\chi_a + \dfrac{5}{4}\right)$, corresponding to the nematic-to-isotropic transition, is defined by the equation

$$1/\Gamma_0^{NI}\phi_r = 4.55 . \tag{8}$$

The nematic phase will be stable, if $1/\Gamma_0 < 1/\Gamma_0^{NI}$. It can be shown that the transition temperature T_{IN} between the isotropic and nematic phases is defined by the equation $\chi_{IN} = \chi(T_{IN}) = \dfrac{1}{\alpha}\cdot\dfrac{4.55 - 1.25 n_r(1 - \phi_p)}{n_r(1 - \phi_p)}$, where $\alpha = \chi_a / \chi$ is the nematic interaction parameter, which is supposed to be independent of the temperature.

The rod-to-rod interaction is supposed to be attractive. Hence, $\chi_a > 0$ and the parameters χ and α have the same sign. The nematic-isotropic phase transition for the different lengths of the ds-DNA rods are presented in Fig. 1.
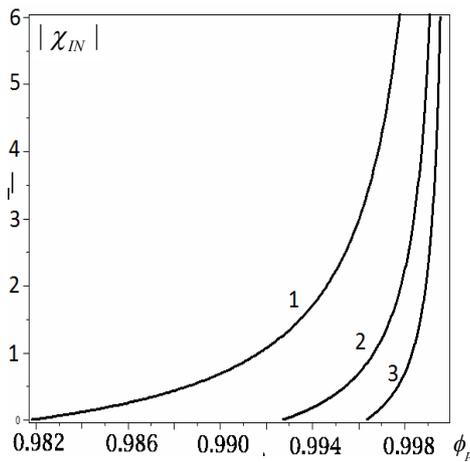
Fig. 1. Dependense of the absolute value of the Flory–Huggins parameter χ_{IN} in on the volume fraction of polymer ϕ_p. Where n_r is equal: 1) $2\cdot10^2$; 2) $5\cdot10^2$; 3) 10^3 and $\alpha = 1.5$.
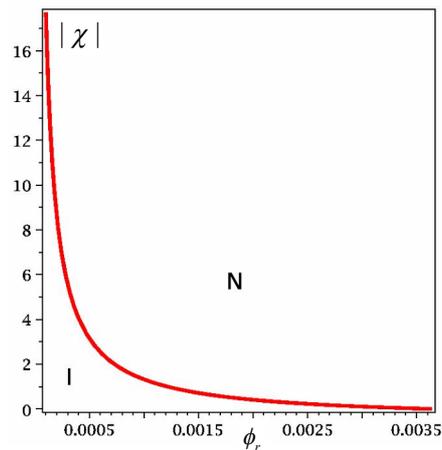
Fig. 2. The phase diagrams of ds-DNAs in the flexible polymer matrix for $n_r = 10^3$. Solid line separates isotropic (*I*) and nematic (*N*) phases.

Conclusion. As we can see from the Eq. (8) and Fig. 1, in the polymer matrix the degree of alignment of the ds-DNAs in the nematic phase is governed by the parameter $\phi_r \Gamma_0 = \dfrac{n_r}{4}(5 + \pi d^3 \chi_{rr})\phi_r$. Thus, by tuning the load of ds-DNAs (ϕ_r) and the rod-to-rod attraction (χ_{rr}), we can obtain different orientationally ordered phases for ds-DNAs with any given aspect ratio n_r. The phase diagram is presented in the Fig. 2.

Thus, liquid crystalline order formation in ds-DNA immeresed in the polymeric matrix occurs with increase of the volume fraction ϕ_r. The volume fraction of transition between isotropic (*I*) and nematic (*N*) phases depends on value of the temperature dependendt Flory–Huggins parameter χ. Hence, the ordered phase formation in ds-DNA is governed by volume fraction of DNA and by temperature. The temperature behavior of the ordered structures in polymers has been extensively investigated before [5, 8]. The difference of the conformational entropy of macromolecules in crystallite and amorphous phases allowed for the free energy of crystallization made it possible to calculate the change of the crystallization rate depending on temperature and obtained a satisfactiry accordance of theory and experiment [8]. The results obtained above clearly show the effect of the polymer matrix on the ordering in DNA molecules. At the same time, at low temperatures bundles of ordered DNAs could serve as a centres of nucleation for the flexible polymer crystallization.

REFERENCES

1. **Drzaic P.S.** Liquid Crystal Dispersions. Singapore: World Scientific, 1995, 448 p.
2. **Crawford G.P., Zumer S.** Liquid Crystals in Complex Geometries. London: Taylor and Francis, 1996, 505 p.
3. **Todd B.A., Rau D.C.** Interplay of Ion Binding and Attraction in DNA Condensed by Multivalent Cations. // Nucleic Acids Res., 2008, v. 36, p. 501–510.
4. **de Gennes P.-G., Prost J.** The Physics of Liquid Crystals. Oxford: Clarendon Press, 1993, 597 p.
5. **Matsuyama A., Kato T.** Theory of Binary Mixtures of a Flexible Polymer and a Liquid Crystal. // J. Chem. Phys., 1996, v. 105, p. 1654–1660.
6. **Grosberg A.Yu., Khokhlov A.R.** Statistical Physics of Macromolecules. New-York: AIP Press, 1994, 350 p.
7. **de Gennes P.-G.** Scaling Concepts in Polymer Physics. Cornell Univ. Press, 1979, 324 p.
8. **Mashoorian A.M., Ovanesov G.T., Grogorian Z.A., Gasparian K.A.** Calculation of the Flexible Chain Polymers Melting Range Dependence on the Crystallization Temperature. // Proceed. Nat. Acad. Sci. Armenia. Physics, 1997, v. 32, p. 316–319 (in Russian).