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Microphase Separation in Randomly Branched Polymers

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ABSTRACT: We study microphase separation between ends and branches in randomly branched globular polymers. The main result of this work is that when the interaction energetics between monomers correspond to strong enough separation, a regular domain structure appears. The period of this structure is calculated. It is large when linear parts of the chain connecting ends and branched points are long.

I. Introduction

Microphase separation is a well-known effect in polymer physics.[1-4] This effect is interesting both from the point of view of possible applications and for fundamental polymer science as it is one of the most pronounced polymeric effects. Polymer bonds prevent macrophase separation between unlike monomers or other elements of a system, and as a compromise between the tendency for segregation and the constraints imposed by polymeric bonds a microphase with a periodic structure evolves. The size of the domains does not depend on the size of a system and is determined by the structure of blocks as in the case of block copolymers.

The case of block copolymers is the most studied (see, e.g., refs 2 and 5 and references given therein). Several mesophases were found, and a detailed theory outlining their stability has been suggested. These effects were discussed for linear molecules which must be chemically heterogeneous in order to form mesophases. Another interesting possibility of mesophase formation exists in branched polymers where this chemical heterogeneity is natural and inevitable; monomers with different functionality—end points, linear parts, and branch points—must interact in a different way so that in this sense any branched polymer is a heteropolymer. Therefore they may tend to separate, leading to peculiar mesophases.

In this paper we will investigate such a separation and will show that if the linear parts of a polymer are long enough a mesophase with large domains enriched by branch points and end points does indeed appear. Our consideration is based on the mean-field approach. The key point in this approach is the calculation of the entropy of an inhomogeneous polymer. We will derive a general formula for the entropy of a branched polymer and, based on that, analyze mesophase formation in that system.

II. Model and Mean-Field Equations

We consider a randomly branched polymer without cycles composed from N monomers of different functionality. We will consider a condensed state of such a molecule (globule or melt). In this case a mean-field approximation is valid.[6] Within this approximation the free energy F must be considered as a function of the densities $\rho_f(\mathbf{r})$ of monomers of different functionalities f. We present this in the form:

$$F\{\rho_f\} = E\{\rho_f\} - TS\{\rho_f\} \tag{1}$$

where $S\{\rho_f\}$ is entropy in which polymeric bonds play a major role and "energy" $E\{\rho_f\}$ is expressed in the usual way through the free energy $F_0\{\rho_f\}$ of a gas of disconnected links[6]

$$E\{\rho_f\} = F_0\{\rho_f\} - F_{\mathrm{id}}\{\rho_f\} \tag{2}$$

where

$$F_{\mathrm{id}}\{\rho_f\} = \sum_{f=1} \int \mathrm{d}\mathbf{r}\ \rho_f(\mathbf{r}) \ln(\rho_f(\mathbf{r})/e) \tag{3}$$

is the ideal gas contribution to the free energy.

The structure of polymeric bonds is described in terms of $g(\mathbf{r}_i - \mathbf{r}_{i-1})$, the probability density to find monomer i at $\mathbf{r}_i$ provided that monomer $i-1$ is at $\mathbf{r}_{i-1}$. The entropy of a branched polymer can be evaluated as (see ref 7 and the Appendix):

$$S\{\rho_f\} = \sum_{f=1} \int \mathrm{d}\mathbf{r}\ \rho_f(\mathbf{r}) \ln\left[\frac{(\hat{g}\phi)^{f-1}\rho}{\phi\rho_f}\right] \tag{4}$$

where $\hat{g}$ denotes the integral operator

$$\hat{g}\phi = \int g(\mathbf{r}-\mathbf{r}')\ \phi(\mathbf{r}')\ \mathrm{d}\mathbf{r}' \tag{5}$$

and $\rho(\mathbf{r}) = \sum_{f=1}\rho_f(\mathbf{r})$ is the total density of all monomers. Function $\phi(\mathbf{r})$ is a solution of the equation

$$\frac{\rho}{\phi} = \sum_{f=2} (f-1)\hat{g}\left(\frac{\rho_f}{\hat{g}\phi}\right) \tag{6}$$

In order to obtain the Landau expansion for the free energy, we consider small deviations of densities $\delta\rho_f(\mathbf{r})$ from their equilibrium values $\bar{\rho}_f$ ($\delta\rho_f(\mathbf{r}) \ll \bar{\rho}_f$). In this case eq 6 can be solved for ϕ:

$$\phi \approx 1 + \bar{\rho}^{-1}(\hat{g}^2 - 1)^{-1} \sum_{f=2} (f-1)\hat{g}\delta_f \tag{7}$$

where δ_f is an abbreviation for $\delta\rho_f(\mathbf{r})$ and incompressibility of the globule (ρ = const) is assumed. This solution must be substituted into the expression (4) for the entropy to give a closed function of the densities only. Expansion to second order in δ_f gives the result

$$S\{\rho_f\} = (2\bar{\rho})^{-1} \int \Big(\sum_f (f-1)\hat{g}\delta_f\Big)(1-\hat{g}^2)^{-1}\Big(\sum_f (f-1)\hat{g}\delta_f\Big)\ \mathrm{d}\mathbf{r} - \frac{1}{2}\sum_f \rho_f^{-1} \int \delta_f^{\,2}\ \mathrm{d}\mathbf{r} \tag{8}$$

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or Fourier transformed:

$$S\{\rho_f(\mathbf{k})\} = \frac{V}{2}\sum_{\mathbf{k}}\left[\bar{\rho}^{-1}\frac{g^2(\mathbf{k})}{1-g^2(\mathbf{k})}\Big(\sum_f (f-1)\delta_f(\mathbf{k})\Big)^2 - \sum_f \bar{\rho}_f^{-1}\delta_f^{\,2}(\mathbf{k})\right] \quad (9)$$

where V is the volume of the system,

$$\delta_f(\mathbf{r}) = \sum_{\mathbf{k}}\delta_f(\mathbf{k})\,\mathrm{e}^{i\mathbf{k}\mathbf{r}}$$

and

$$g(\mathbf{k}) = \int \mathrm{d}\mathbf{r}\,g(\mathbf{r})\,\mathrm{e}^{i\mathbf{k}\mathbf{r}}$$

We may also expand the energy $E\{\rho_f\}$ in eq 2 in powers of small deviations δ_f:

$$E\{\rho_f\} = E_0 + \frac{V}{2}\sum_{\mathbf{k}}\sum_{f_1,f_2}B_{f_1f_2}(\mathbf{k})\,\delta_{f_1}(\mathbf{k})\,\delta_{f_2}(\mathbf{k}) \quad (10)$$

where $E_0 = E\{\bar{\rho}_f\}$.

We consider the case where only end points ($f = 1$), linear parts ($f = 2$), and branch points ($f = 3$) are present. In this case the number of end points N_1 for the branched molecule without cycles is equal in the thermodynamic limit to the number of branch points N_3 ($N_1 = N_3 + 2 \approx N_3$); i.e., $\bar{\rho}_3 = \bar{\rho}_1$. Moreover, incompressibility imposes another constraint: $\delta_2 = -(\delta_1 + \delta_3)$ and therefore $\sum_f (f-1)\delta_f = \delta_3 - \delta_1$. This means that the expressions for energy and for entropy can be further simplified:

$$S = \frac{V}{2}\sum_{\mathbf{k}}\left[\frac{g^2(\mathbf{k})}{1-g^2(\mathbf{k})}(\delta_3(\mathbf{k})-\delta_1(\mathbf{k}))^2 - \frac{1}{2\bar{\rho}_1}(\delta_3(\mathbf{k})-\delta_1(\mathbf{k}))^2 - \left(\frac{1}{2\bar{\rho}_1}+\frac{1}{\bar{\rho}_2}\right)(\delta_3(\mathbf{k})+\delta_1(\mathbf{k}))^2\right] \quad (11)$$

$$E = \frac{V}{2}\sum_{\mathbf{k}}[B_-(\mathbf{k})\,(\delta_3(\mathbf{k})-\delta_1(\mathbf{k}))^2 + B_+(\mathbf{k})\,(\delta_3(\mathbf{k})+\delta_1(\mathbf{k}))^2] \quad (12)$$

In this simplified representation only two independent modes are possible: $\delta_-(\mathbf{k}) = \delta_3(\mathbf{k}) - \delta_1(\mathbf{k})$ and $\delta_+(\mathbf{k}) = \delta_3(\mathbf{k}) + \delta_1(\mathbf{k})$. The δ_- mode corresponds to separation, while the equilibrium value of δ_+ must be 0. Therefore the free energy from eqs 12 and 11 can be taken as

$$F = E - TS = \frac{V}{2}\sum_{\mathbf{k}}G(\mathbf{k})\,\delta_-^{\,2}(\mathbf{k}) \quad (13)$$

where

$$G(\mathbf{k}) = B_-(\mathbf{k}) + \frac{T}{2\bar{\rho}_1} + \frac{T}{\bar{\rho}}\frac{g^2(\mathbf{k})}{1-g^2(\mathbf{k})} \quad (14)$$

III. Formation of the Mesophase

It is clear that, if $G(\mathbf{k}) > 0$ for any $\mathbf{k}$, the equilibrium value of δ_- is zero; i.e., there is no separation. At the same time, if $G(\mathbf{k}) < 0$ at some $\mathbf{k}$, the corresponding modes become unstable and an inhomogeneous phase emerges. In this case the equilibrium values for δ_- are determined by higher order terms in the Landau expansion for free energy. However, the transition point is determined, as usual, by the equation

$$\min_{\mathbf{k}} G(\mathbf{k}) = 0$$

and the size of the domains in the inhomogeneous phase is determined by the wavevectors $\mathbf{k}^*$ at which the function $G(\mathbf{k})$ has a minimum. In this case the characteristic size of a microdomain structure $R \sim |\mathbf{k}^*|^{-1}$. It should be noticed right away that the instability at nonzero wavevector $\mathbf{k}$ is a pure polymeric effect in our system: if the term with $g(\mathbf{k})$ does not appear in eq 14, then $G(\mathbf{k})$ can reach minimum only at $\mathbf{k}^* = 0$. In this case the system would undergo macrophase separation. On the other hand, chain connectivity prevents macrophase separation because $G(\mathbf{k}) \to \infty$ as $\mathbf{k} \to 0$ since $g(\mathbf{k}) \to 1$ as $\mathbf{k} \to 0$. (We remind the reader that g has the meaning of probability density[6] and as such it is normalized.)

It is expected that when linear parts of the chain are long enough (i.e., $N_2 \gg N_1$ and $\bar{\rho}_2 \sim \bar{\rho} \gg \bar{\rho}_1$), the size of microdomains $R \sim |\mathbf{k}^*|^{-1}$ is much larger than monomer size a. In this case all interesting effects occur at small $\mathbf{k}$ and we can expand:

$$B_-(\mathbf{k}) \sim B_0 + \sigma^2\mathbf{k}^2$$

$$g(\mathbf{k}) \sim 1 - a^2\mathbf{k}^2$$

where the term $\sigma^2\mathbf{k}^2$ corresponds to surface tension energy. In this case the function

$$G(\mathbf{k}) = \left(B_0 + \frac{T}{2\bar{\rho}_1}\right) + \sigma^2\mathbf{k}^2 + \frac{T}{2\bar{\rho}a^2\mathbf{k}^2} \quad (15)$$

reaches a minimum at

$$|\mathbf{k}| = |\mathbf{k}^*| = \left(\frac{T}{2\bar{\rho}a^2\sigma^2}\right)^{1/4} \quad (16)$$

and the minimum of $G(\mathbf{k})$ is

$$G(\mathbf{k}) = \left(B_0 + \frac{T}{2\bar{\rho}_1}\right) + \frac{\sigma}{a}\left(\frac{2T}{\bar{\rho}}\right)^{1/2} \quad (17)$$

therefore transition to the inhomogeneous phase takes place when

$$\left(B_0 + \frac{T}{2\bar{\rho}_1}\right) = -\frac{\sigma}{a}\left(\frac{2T}{\bar{\rho}}\right)^{1/2} \quad (18)$$

i.e., at a lower value of B_0 than in the system of disconnected links which means simply that polymeric bonds prevent separation.

We have to verify now that separation indeed occurs at large scales, or at small $\mathbf{k}$. Indeed for the surface tension $\sigma^2 \sim a^2T/\bar{\rho}_1$, and therefore from eq 16 it follows that $|\mathbf{k}^*|a \sim (\bar{\rho}_1/\bar{\rho}) \ll 1$. This justifies the expansion in $\mathbf{k}$.

IV. Discussion

We showed the possibility of a new type of mesophase in the polymeric system—microphase separation of branch points and end points in branched polymers. This phase occurs when there is a strong repulsion between end points and branches. We estimated the characteristic scale at which separation occurs and showed that this scale is large when there are long linear parts between the end points and branches.

The physical reason for such a separation is clear. Polymer bonds prevent separation at the macroscale, while surface tension does not allow separation on the smallest possible scale. As a result of such competition we obtain stabilization at nonzero $\mathbf{k}^*$ and domain structure. It should be noted that the physics of this effect is similar to that of block copolymers.[2]

In this paper we demonstrated only the possibility of microphase separation in branched polymers and estimated the corresponding size of a microdomain. In order to analyze the symmetry of a mesophase and its structure (lamellar, micellar, etc.), the Landau expansion should be further extended to include higher order terms which provide stabilization and determine possible combinations of wavevectors of density variation at which the system may be stable. This procedure is analogous to the one suggested in ref 2. Results of this analysis will be published elsewhere.

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Appendix. Calculation of the Configurational Entropy

Calculation of entropy $S\{\rho_f\}$ is based on two approaches: the Lifshitz method for linear polymers[6] and the recursion relation for the partition function for branched polymers derived by de Gennes.[8] Here we present only the main steps of the calculation; details are given in ref 7.

In accordance with the general approach to entropy calculation, we consider a branched polymer in an external field $\varphi_f(\mathbf{r})$. The partition function of this system can be written as an integral over the densities $\rho_f(\mathbf{r})$:

$$Z\{\varphi_f\} = \int D\rho_f(\mathbf{r}) \exp(-\sum_{f=1} \int \varphi_f(\mathbf{r})\, \rho_f(\mathbf{r})\, \mathrm{d}\mathbf{r} + S\{\rho_f\}) \quad (19)$$

In the mean-field approximation this integral can be evaluated by the saddle-point method with the result:

$$S\{\rho_f\} = \sum_f \int \rho_f(\mathbf{r})\, \varphi_f(\mathbf{r})\, \mathrm{d}\mathbf{r} + \ln Z\{\varphi_f\} \quad (20)$$

with $\varphi_f(\mathbf{r})$ determined by the equation

$$\varphi_f(\mathbf{r}) = \frac{\delta S\{\rho_f\}}{\delta \rho_f(\mathbf{r})}$$

and

$$\rho_f(\mathbf{r}) = -\frac{\delta \ln Z\{\varphi_f\}}{\delta \varphi_f(\mathbf{r})} \quad (21)$$

Thus the entropy can be obtained from eqs 21 and 19 provided that we can calculate the partition function $Z\{\varphi_f\}$. We introduce a new object $G_N(\mathbf{r})$—the partition function of a polymer of N monomers with one monomer (which we call the root monomer) fixed at point $\mathbf{r}$. For this partition function a simple recurrence relation holds:

$$G_N(\mathbf{r}) = \sum_{f=2} \Lambda_f \int \mathrm{d}\mathbf{r}'\, g(\mathbf{r}-\mathbf{r}')\, \mathrm{e}^{-\varphi_f(\mathbf{r}')} \sum_{i_1, i_2, \ldots, i_{f-1} > 1} G_{i_1}(\mathbf{r}')\, G_{i_2}(\mathbf{r}') \ldots G_{i_{f-1}}(\mathbf{r}') \times \Delta(i_1 + \ldots + i_{f-1} - f + 2 - N) \quad (22)$$

where Λ_f is the probability that a given root monomer is connected to a monomer with functionality f and $\Delta(i) = 1$ if $i = 0$ and 0 otherwise. Introducing the generating function $G_p(\mathbf{r}) = \sum_{N=2}^{\infty} p^{N-1} G_N(\mathbf{r})$, we transform eq 22 into

$$G_p(\mathbf{r}) = p \sum_{f=1} \Lambda_f \hat{g}(\mathrm{e}^{-\varphi_f} G_p^{\,f-1}) \quad (23)$$

where the operator $\hat{g}$ is defined by eq 5. In analogy with ref 8 we expect that G_p has a square root singularity as a function of p:

$$G_p(\mathbf{r}) = \Psi(\mathbf{r})\, (p^* - p)^{1/2} + \text{regular part} \quad (24)$$

therefore in thermodynamic limit $N \to \infty$

$$Z\{\varphi_f\} \approx G_N(\mathbf{r}) \approx (p^*)^{-N} \quad (25)$$

Differentiating eq 23 with respect to p and taking the singular part only, we obtain

$$\Psi(\mathbf{r}) = p^* \sum_{f=2} \Lambda_f (f-1) \hat{g}(\mathrm{e}^{-\varphi_f} \Phi^{f-2} \Psi) \quad (26)$$

where $\Phi(\mathbf{r}) = \lim_{p \to p^*} G_p(\mathbf{r})$. Variation of eq 23 with respect to $\varphi_f(\mathbf{r})$ at $p = p^*$ together with eqs 21, 25, and 26 yields

$$\rho_f(\mathbf{r}) = C \Lambda_f \mathrm{e}^{-\varphi_f(\mathbf{r})} \Phi^{f-1} \Psi(\mathbf{r}) \quad (27)$$

where

$$C = N[\sum_{f=2} (f-1) \Lambda_f \int \mathrm{d}\mathbf{r}\, \mathrm{e}^{-\varphi_f(\mathbf{r})} \Phi^{f-1} \Psi(\mathbf{r})]^{-1} \quad (28)$$

Expressing $\varphi_f(\mathbf{r})$ and substituting the result into eqs 20, 23, and 26, we obtain

$$S\{\rho_f\} = \sum_{f=1}^{\infty} \rho_f \ln\left[\frac{C \Lambda_f \Phi^{f-2} \Psi}{\rho_f} \hat{g}\left(\frac{\rho}{\Psi}\right) \right] \quad (29)$$

with $\Phi = (p^*/C)\hat{g}(\rho/\Psi)$ and

$$\Psi = \sum_{f=2} (f-1) \hat{g}\left(\frac{\rho_f}{\hat{g}(\rho/\Psi)} \right) \quad (30)$$

Introducing the new function $\phi = \rho/\Psi$ and removing trivial, conformation-independent terms, we have the final expression for entropy (eq 4).

References and Notes

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