Thermodynamic prediction of molecular morphology of amorphous regions of drawn semicrystalline polymers

M. G. Zaitsev* and S. E. Varyukhin
Department of Physics, Moscow State Pedagogical University, Malaya Pirogovskaya 1, 119882 Moscow, Russia
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The molecular morphology of amorphous regions of drawn semicrystalline polymers is calculated assuming a minimum of the free conformational energy, provided that crystallite and amorphous region thicknesses and density ratio and macromolecule elongation due to polymer drawing are given parameters. The proportions of regular folds, adjacent re-entrant and random re-entrant loops, and tie chains and the length distributions of these subchains are calculated as functions of the amorphous region thickness and macromolecule elongation. Using a Monte-Carlo simulation, the distribution of local density within the amorphous region was studied, and introduction into the theory of an interfacial layer between the crystallite and amorphous regions where possible conformations of subchains are limited was substantiated.

(Keywords: semicrystalline polymer; morphology; thermodynamics; tie chains; loops; re-entry; drawing; simulation)

INTRODUCTION

Melt crystallization and drawing of a polymer always result in the emergence of a heterogeneous structure containing alternating crystallites and amorphous regions of the order of 100 Å[1,2]. Molecular morphology must depend, on the one hand, on the parameters of the emerging structure and the conditions under which crystallization occurs (or recrystallization processes on polymer deformation)[3]. On the other hand, it is the amorphous regions of semicrystalline polymers that may cause these structural parameters, thus limiting the crystallization process. In addition, the molecular morphology of the amorphous regions of semicrystalline polymers governs to a considerable extent their mechanical properties[4,5]. Therefore, experimental and theoretical study of the molecular morphology of amorphous regions of semicrystalline polymers is an important problem of polymer physics.

If the molecular weight of the polymer is high enough, then the probability of finding free ends of macromolecules in the amorphous region is low. Each macromolecule crosses several crystalline and amorphous regions. Polymer segments in the amorphous region are anchored at the crystallite surfaces. These segments are hereafter referred to as subchains. Three kinds of such subchains are distinguished: loops, tie chains and cilia. Depending on the length and arrangement of loop attachment points over the crystallite surface, three kinds of loops are distinguished:

(1) regular folds – the shortest loops with adjacent re-entry;
(2) adjacent re-entrant loops of arbitrary length; and
(3) long random re-entrant loops (*Figure 1b*).

One of the main problems in the investigation of molecular morphology of amorphous regions is the determination of the proportion of folds, loops and tie chains and their length distributions.

To solve this problem, some authors[6–8] simulated the subchains in the amorphous region by means of a random-walk model where the walk proceeds between absorbing planes – namely the surfaces of crystallites. A detailed investigation was carried out in ref. 9, where the chain behaviour in the amorphous region of a semicrystalline polymer was compared with the gambler's ruin problem known in mathematics. The formulae given there make it possible to calculate the proportions and length distributions of loops and tie chains as functions of the amorphous layer thickness.

Various versions of the gambler's ruin problem have been used for the theoretical investigation of molecular morphology of the folded surface of crystallites. The most acute problem here has long been the problem of the relationship between proportions of regular fold, or, in more general terms, of adjacent re-entrant loops and long random re-entrant loops. The solution of this problem governs the choice between the regular folded crystallization model[10] now being actively developed by Hoffman *et al.*[11–13] and Flory's switchboard model[6,14–16]. After long and detailed discussion[17–24] the following consensus appears to be achieved in this problem: the proportion of adjacent re-entrant loops ranges from 70% to 80%, with the greater part of them being regular folds.

Different data are now available on the problem of the proportions and length distributions for the tie chains and long loops[9,21,23].

Interesting thermodynamic approaches to the prediction of the molecular morphology of the amorphous regions of semicrystalline polymers were developed elsewhere[25,26]. However, the authors of both publications

*To whom correspondence should be addressed

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do not introduce any limitations on the value of the amorphous region density. As a result, a temperature change of several tens of degrees causes a three- to four-fold change in the average subchain length. It is natural that the density of the amorphous region changes too, which does not allow these results[25,26] to be considered realistic. Besides, the problem of the relationship between the proportions of folds, loops and tie chains was not considered in these papers.

Finally, none of the above publications[6–9,17–26] took into account chain extension on polymer drawing and hence none of them considered the effect of the latter on the molecular morphology of the amorphous region.

The purpose of the present publication is to predict the molecular morphology of the amorphous region of a drawn polymer on the basis of minimization of its equilibrium conformational free energy at fixed sizes of crystallites c and amorphous regions a, with due regard to the real ratio of their densities (d_a/d_c) and the degree of chain extension characterizing the drawing ratio.

In the next section we formulate the principal equations of the theory, which can be solved numerically. We assume that subchains in amorphous regions are ideal and realize their possible conformations independently of one another. We take into account the subchain volume by introduction of the constant ratio of densities d_a/d_c.

In the third section the results of a Monte-Carlo calculation of local density within the amorphous region are presented. This calculation is based on subchain length distributions that have been obtained in the previous part of the paper. It reveals a great density excess in the vicinity of the crystallite surface. To eliminate this defect, an interfacial layer between the crystalline and amorphous region where the possible conformations of subchains are limited is introduced into the theory.

The results of calculation of the parameters of molecular morphology of the amorphous region with due regard to the interfacial layer are presented in the fourth section of the paper. Finally, we briefly discuss the results and the foundation of the theory.

THEORY: PRINCIPAL EQUATIONS

Let us consider a macromolecule of length L in the stacked-lamellar model with lamellae of thickness c, separated by amorphous regions of thickness a (*Figure 1*). Assume that the distance between the macromolecule ends (end-to-end distance) is constant and equal to R. The ratio R/L characterizes the chain extension of the macromolecule due to polymer drawing.

The molecular morphology of the amorphous region is assumed to correspond to a minimum of the free conformational energy under some given limitations, namely under given parameters of supermolecular structure a and c, the degree of macromolecule extension R/L and ratio d_a/d_c. In other words, the polymer system is assumed to have enough time to achieve local thermodynamic equilibrium compatible with the given limitations during melt crystallization and formation of lamellar or microfibrillar structure.

So we should write down the expression for the total free conformational energy of all subchains of the macromolecule in the stacked-lamellar model as a function of the statistical weights of the different types of subchains and minimize it.

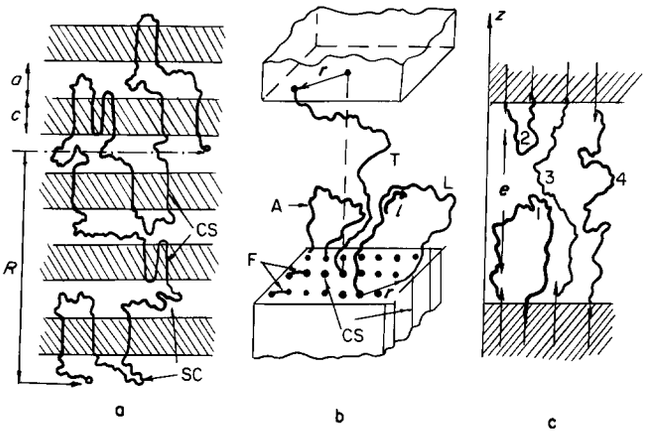

Figure 1 Macromolecule in stacked-lamellar model. (a) Characteristics: c = thickness of crystalline lamella; a = thickness of amorphous region; R = end-to-end distance of macromolecule; SC, subchains in amorphous region; CS, crystal stems. (b) Different types of subchains: F, regular folds; A, adjacent re-entrant loops; L, random re-entrant loops; T, tie chains; r, l = parameters of subchain state (see text). (c) The z axis of drawing; e = unit vector of macromolecule orientation; 1–4, types of subchains, determined in the theory (see text)

Table 1 Permissible order of alternation of subchains of different types

	n_{i+1}			
n_i	1	2	3	4
1	No	Yes	No	Yes
2	Yes	No	Yes	No
3	Yes	No	Yes	No
4	No	Yes	No	Yes

Let us imagine the macromolecule as a sequence of crystal stems and subchains (loops and tie chains) in amorphous regions (*Figure 1a*). There is one subchain for each crystal stem. The presence of the free ends can be neglected if we consider that L is sufficiently large. Let us determine the unit vector $\boldsymbol{e}$ at each point of the macromolecule, which determines its orientation. Let us determine four types of subchains (*Figure 1c*). If the projection of $\boldsymbol{e}$ on the z axis is positive at the point of exit from the crystallite, and negative at the entry point, we have a subchain of type 1 (loop). If vice versa, we have a subchain of type 2 (loop). If the projection of $\boldsymbol{e}$ on the z axis is positive at both the exit and entry points, we have a subchain of type 3 (tie chain). If both are negative, we have a subchain of type 4 (tie chain). It is clear that subchains of different types cannot follow one another arbitrarily. Their permissible sequence is given in *Table 1*, which indicates whether or not the $(i+1)$th subchain can have the type n_{i+1}, if the ith one had the type n_i. It is clear that the numbers of subchains of the first and second types N_1 and N_2 cannot differ from each other by more than ± 1. Since the total number of subchains in the macromolecule is considered to be large enough, we can write down approximately:

$$N_1 = N_2 \tag{1}$$

Then, it is evident that the end-to-end distance is determined by the difference between the numbers of subchains of the third and fourth types (*Figure 1a*):

$$N_3 - N_4 = R/(a+c) \tag{2}$$

The total number of subchains (and crystal stems) in the macromolecule is evidently equal to:

$$N_c = L/(c + \bar{l}) \tag{3}$$

where $\bar{l}$ is the average length of the subchain in the amorphous region; $\bar{l}$ is rigidly coupled with the density ratio d_a/d_c between the amorphous region and the crystallite. Actually:

$$\bar{l} = (d_a/d_c)a \tag{4}$$

As the configuration of the macromolecule changes in the stacked-lamellar model, the type of the ith subchain n, the projection of the distance between the points of entry and exit of the subchain into and from crystallites on the plane of the crystallite surface $\boldsymbol{r}$ and the length l of the subchain can change (*Figure 1b*). We shall characterize the subchain state by the set of variables $\{n, \boldsymbol{r}, l\}$ and shall search for the statistical weights of subchain states $\rho(n, \boldsymbol{r}, l)$. Each given state of subchains $\{n, \boldsymbol{r}, l\}$ has its own free conformational energy F_s depending on whether the subchain is a loop ($n = 1, 2$) or a tie chain ($n = 3, 4$) and on the distance $\boldsymbol{r}$ and the subchain length l: $F_s(n, \boldsymbol{r}, l)$.

If $F_s(n, \boldsymbol{r}, l)$ is known, the free conformational energy of the macromolecule F can be written as a function of the statistical weights $\rho(n, \boldsymbol{r}, l)$:

$$F = \sum_{n,\boldsymbol{r},l} \rho(n, \boldsymbol{r}, l) F_s(n, \boldsymbol{r}, l) - TS \tag{5}$$

where S is the entropy associated with all permissible rearrangements of subchains in the set of states $\{n, \boldsymbol{r}, l\}$. It is not difficult to see that all the rearrangements of the subchains of type n give a contribution to the entropy:

$$S_n/kN_c = -\sum_{\boldsymbol{r},l} \rho(n, \boldsymbol{r}, l) \ln \rho(n, \boldsymbol{r}, l) + v_n \ln v_n \tag{6}$$

where $v_n = N_n/N_c$ is the proportion of chains of type n and k is the Boltzmann number. It is necessary to add here the contribution to the entropy associated with permissible rearrangements of subchains of different types within the macromolecule. The total number of different sequences of the subchain is equal to:

$$\frac{N_c!}{N_1!\,N_2!\,N_3!\,N_4!}$$

However, among them there are sequences that contain a prohibited order of sequence of elements (see *Table 1*).

Let us estimate the proportion of permissible sequences of subchains. The probability of meeting a prohibited subchain with $n = 1$ or $n = 3$ following a subchain of the first type is equal to $(N_1 + N_3)/N_c$. The probability of not meeting them after all subchains of the first type is apparently:

$$[(N_2 + N_4)/N_c]^{N_1}$$

Reasoning in the same way with respect to the other prohibited pairs of subchains, let us estimate approximately the number of permissible sequences:

$$\Gamma = \frac{N_c!}{N_1!\,N_2!\,N_3!\,N_4!} \frac{(N_2 + N_4)^{N_1+N_4}(N_1 + N_3)^{N_2+N_3}}{N_c^{N_c}}$$

and the corresponding contribution to the entropy:

$$\begin{aligned} S_{mix}/kN_c = {} & v_1[\ln(v_2 + v_4) - \ln v_1] \\ & + v_2[\ln(v_1 + v_3) - \ln v_2] \\ & + v_3[\ln(v_1 + v_3) - \ln v_3] \\ & + v_4[\ln(v_2 + v_4) - \ln v_4] \end{aligned} \tag{7}$$

Combining equations (5)–(7) we have the expression for the free conformational energy of the macromolecule:

$$\begin{aligned} F/N_c = {} & \sum_{n,\boldsymbol{r},l} \rho(n, \boldsymbol{r}, l) F_s(n, \boldsymbol{r}, l) + T \sum_{n,\boldsymbol{r},l} \rho(n, \boldsymbol{r}, l) \ln \rho(n, \boldsymbol{r}, l) \\ & - T[(v_2 + v_3)\ln(v_1 + v_3) + (v_1 + v_4)\ln(v_2 + v_4)] \end{aligned} \tag{8}$$

It is necessary to find the minimum of F as a function of $\rho(n, \boldsymbol{r}, l)$ under the following conditions:

$$\sum_{n,\boldsymbol{r},l} \rho(n, \boldsymbol{r}, l) = 1 \tag{9}$$

$$\sum_{n,\boldsymbol{r},l} l\rho(n, \boldsymbol{r}, l) = \bar{l} \tag{10}$$

$$\sum_{\boldsymbol{r},l} [\rho(1, \boldsymbol{r}, l) - \rho(2, \boldsymbol{r}, l)] = 0 \tag{11}$$

$$\sum_{\boldsymbol{r},l} [\rho(3, \boldsymbol{r}, l) - \rho(4, \boldsymbol{r}, l)] = \frac{R}{L}\frac{\bar{l} + c}{a + c} \tag{12}$$

Formulae (9) and (10) are the condition of normalization and the condition of constancy of the average length of the subchain (actually, the condition of constancy of the density of the amorphous region); and formulae (11) and (12) are conditions (1) and (2) rewritten with the use of statistical weights $\rho(n, \boldsymbol{r}, l)$ and formula (3). Minimizing F by the Lagrange multiplier method and using conditions (9)–(12), we obtain after elementary transformation the expression for statistical weights and proportions of subchains of various types:

$$\rho(n, \boldsymbol{r}, l) = \frac{\lambda_n}{Z} \exp\left[-\frac{F_s(n, \boldsymbol{r}, l) + \beta l}{kT}\right] \tag{13}$$

$$v_1 = v_2 = \frac{\bar{l}_T - \bar{l}}{2(\bar{l}_T - \bar{l}_L)} \tag{14}$$

$$v_{3,4} = \frac{1}{2}\left\{\frac{\bar{l} - \bar{l}_L}{\bar{l}_T - \bar{l}_L} \pm \left[\left(\frac{\bar{l} - \bar{l}_L}{\bar{l}_T - \bar{l}_L}\right)^2 - \frac{S_3^2}{S_1^2}\left(\frac{\bar{l}_T - \bar{l}}{\bar{l}_T - \bar{l}_L}\right)^2\right]^{1/2}\right\} \tag{15}$$

where

$$\bar{l}_T = S_{l_3}/S_3 \qquad \bar{l}_L = S_{l_1}/S_1 \tag{16}$$

are the average lengths of tie chains and loops,

$$\lambda_1 = \lambda_2 = 1 \qquad \lambda_3 = 1/\lambda_4 = (v_3/v_4)^{1/2} \tag{17}$$

$$Z = 2S_1 + (\lambda_3 + \lambda_4)S_3 \tag{18}$$

$$S_n = \sum_{l,\boldsymbol{r}} \exp\left[-\frac{F_s(n, \boldsymbol{r}, l) + \beta l}{kT}\right]$$

$$S_{l_n} = \sum_{\boldsymbol{r},l} l \exp\left[-\frac{F_s(n, \boldsymbol{r}, l) + \beta l}{kT}\right] \qquad n = 1, 3 \tag{19}$$

Summation in (19) is performed over all sites of the crystallite surface and for all values of l beginning from

$l_{min}^{(n)}$. For loops ($n = 1$), $l_{min}^{(1)}$ is the length of a regular fold; for tie chains ($n = 3$), $l_{min}^{(3)} = (a^2 + r^2)^{1/2}$.

The parameter β is a function of the value of molecule elongation R/L (at fixed values of a, c, d_a/d_c and T) and can be found by numerical solution of equation (12) after substitution into it of formulae (15), (16) and (19).

Formulae (12)–(19) are applicable to any flexible-chain semicrystalline polymer to a degree depending on whether the assumptions of the correlation between molecular morphology and the local minimum of free conformational energy and of the independence of conformations of different subchains are correct. To carry out numerical calculations it is necessary to find the particular expression for the free conformational energy of a subchain $F_s(n, r, l)$.

In the present study we use for $F_s(n, r, l)$ the results of the Monte-Carlo calculation and the approximations obtained in ref. 27. It was shown there that for polyethylene subchains (for both loops and tie chains) in the amorphous region $F_s(n, r, l)$ can be approximated by the expression:

$$F_s(n, r, l) = F_{min}(n, l)[A + B\exp(\gamma x^2)] \quad (20)$$

where for the loops

$$x = r/l \quad (21)$$

$$F_{min} = 1035 - (7.1625 - 36l^{-0.79})(T + 28) \quad \text{J mol}^{-1}\ \text{CH}_2$$

and for the tie chains

$$x = (a^2 + r^2)^{1/2}/l \quad (22)$$

$$F_{min} = 1192 - (7.1625 - 40l^{-0.89})(T + 50) \quad \text{J mol}^{-1}\ \text{CH}_2$$

Here

$$\gamma = 2.348 + 8355l^{-1.363} \quad (23)$$

$$B^{-1} = \exp(\gamma) - 1 \qquad A = -1 - B \quad (24)$$

For loops of length 5–12 CH_2 units and for long tie chains where the mean-square vector of length $\langle r^2(l)\rangle^{1/2}$ is greater than the thickness of the amorphous region, approximations (26)–(31) are inapplicable and it is necessary to use numerical data of the Monte-Carlo calculation[27].

According to theoretical[28–30] and experimental[31] publications a loop of five CH_2 units is considered as the minimum possible one and is regarded as a regular fold.

The method described in ref. 27 makes it possible to calculate the free conformational energy F_s of a subchain on a diamond-type lattice. The distances between the crystalline stems on the crystallite surface of polyethylene (PE) differ from those in the diamond-type lattice. In the calculation of F_s for the shortest loops we took into account only those conformations for which the end-to-end distances differ from the permissible distances on the PE crystal surface by not more than 0.25 Å.

So numerical solution of equations (12)–(19) was obtained, using the expressions of $F_s(n, r, l)$ given by formulae (20)–(24) and by the Monte-Carlo method[27].

LOCAL DENSITY WITHIN THE AMORPHOUS REGION

In deriving principal theoretical formulae (12)–(19) it was assumed that the average density of the amorphous region was constant (equation (10)). However, this did not guarantee the constancy of the local density, i.e. the absence of layers with density higher or lower than the average one. To control the local density we carried out a Monte-Carlo simulation of subchains of polyethylene in the amorphous region limited by parallel planes – crystallite surfaces – according to statistical weights (equation (13)) (where β is obtained by numerical solution of equation (12)) and calculated the local density distribution within the amorphous region.

To calculate the contribution of subchains of length $l > 12\ CH_2$ units to the local density, their conformations in the amorphous region were simulated on a computer by means of the random-walk model on a diamond-type lattice between absorbing walls – crystallite faces – just as was done in ref. 33. If random walks have their end on the same wall as where they started, we have a loop; if on the opposite side, a tie chain. The probabilities of different directions of steps on the lattice δ were calculated from the formula:

$$P = -\exp(-E_l/RT)\exp[\alpha(z\cdot\delta)] \quad (25)$$

where E_l is the energy of different conformers of the polyethylene chain according to ref. 34, z determines the direction of the orientation axis and α is the factor reflecting the asymmetry of random walks.

The choice of the value of α depends on the elongation of the macromolecules of PE and is dictated by the following considerations.

The probability of one or another subchain being met in the amorphous layer $\rho(n, r, l)$ must be determined from formulae (12)–(19). Let $\Delta d(x; n, r, l)$ be the contribution to the local density of the subchain in the state $\{n, r, l\}$ averaged over all possible conformations and let x be the distance from the crystallite surface. Then, the local density is apparently equal to:

$$d(x) = \sum_{n,r,l} \Delta d(x; n, r, l)\rho(n, r, l) \quad (26)$$

It is clear that simulating the subchain by symmetric or asymmetric random walks we obtain a statistical distribution $\rho_w(n, r, l)$ generally different from that obtained from our theory. If the computer simulation yields the total summed contribution to the local density of all the subchains built in the state close to $\{n, r, l\}$ equal to $d_w(x; n, r, l)$, then the local density predicted by our theory can be estimated from the formula:

$$d(x) = \sum_{n,r,l} d_w(x; n, r, l)\frac{\rho(n, r, l)}{\rho_w(n, r, l)} \quad (27)$$

To decrease the variance of this estimate (and hence to decrease the required statistics) it appears necessary to select the random walk asymmetry factor so that $\rho_w(n, r, l)$ should be as close as possible to $\rho(n, r, l)$.

For short loops with length $5 < l < 12$ (CH_2 units) the value of $d_w(x; n, r, l)$ was calculated on a computer directly, taking into account all possible conformations.

Practically, for estimation of the local density distribution, the amorphous region of thickness $a = 100$ Å was divided into 20 layers. Statistical weights $\rho(n, r, l)$ and $\rho_w(n, r, l)$ are axially symmetric relative to r. Hence, r can be substituted with $|r|$ and $\rho_w(n, r, l)$ can be estimated by means of two-dimensional histograms separately for the loops $\rho^L(r, l)$ and tie chains $\rho^T(r, l)$. Values of histogram intervals $\Delta r\,\Delta l$ were selected so that

in each interval there are not less than 10 subchains. Altogether, to obtain one local density distribution, about 10^5 various subchains were simulated. The local density distributions $d(x)$ were calculated for the various values of macromolecule elongation R/L. The average density of the amorphous region was assumed to be constant and equal to $d_a = 0.85d_c$ (d_c is the crystallite density).

Figure 2 presents the calculated local density distributions within the amorphous layer at various drawing ratios R/L.

In slightly oriented polymer ($R/L = 0.2$) the density of the layer adjoining the crystallite surface exceeds the density of the crystallite by a factor of 2.1 (*Figure 2a*). As R/L increases, the value of the density excess decreases, but even at $R/L = 0.7$ it is still more than 20% (*Figure 2e*). The density excess in this layer results in a deficiency of density in the middle of the amorphous region.

Flory[22] noted that the density excess in the intermediate layer between the crystallite and the amorphous region in various models can be explained by the assumption of the possibility for each subchain to realize all possible conformations independently of other chains. In such a case, it is natural to weaken this assumption in our theory and take into account the fact that the conformations of the subchain must be limited near the crystallite surface.

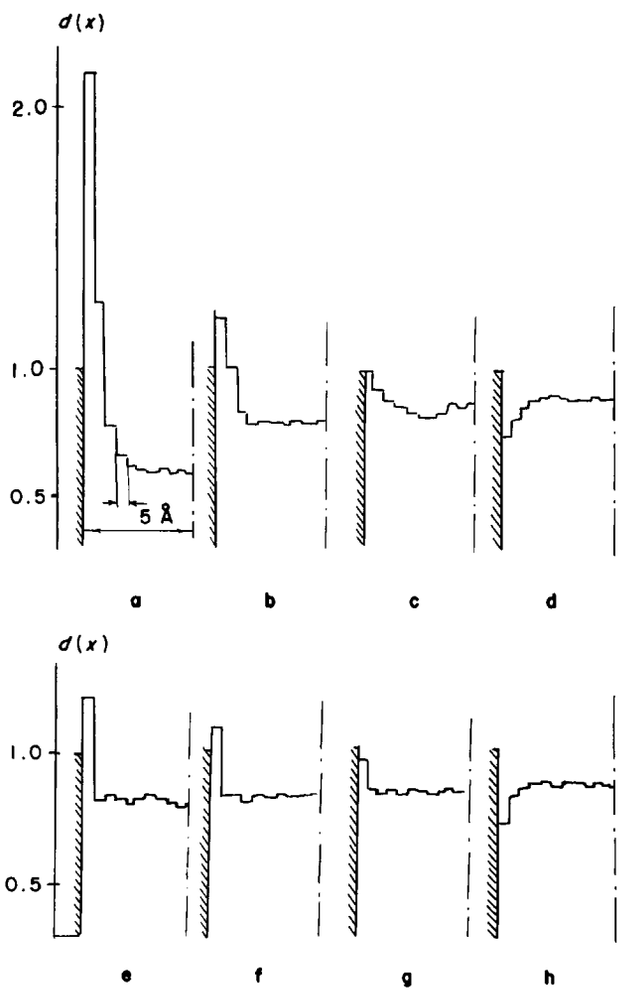

Figure 2 Local density distributions within amorphous region at various values of R/L and various thicknesses of interfacial layer l_s (in CH_2 units): $c = a = 100$ Å; temperature 360 K; $R/L = 0.2$, $l_s = 0$ (a), 2 (b), 3 (c), 4 (d); $R/L = 0.7$, $l_s = 0$ (e), 2 (f), 3 (g), 4 (h). The distributions are symmetric relative to the middle of the amorphous region

Assume that tie chains and long random re-entrant loops retain *trans* condformation at a distance l_s from the crystallite surface.

Let the adjacent re-entrant loops retain this conformation at such a distance $l < l_s$ that the remaining free section is not less than five CH_2 units in length. The shortest loops of length 5–6 CH_2 units still realize all possible conformations. As a result of such modification of the theory, an interfacial layer of thickness l_s is formed where the unit orientation degree decreases gradually.

Limitation of possible conformations of tie chains and long loops is easy to take into account in the theory being developed. *Trans* sequences of length l_s within the interfacial layer, which are included in tie chains and long random re-entrant loops, do not contribute to the free conformational energy $F_s(n, r, l)$ of these subchains, but still contribute to average lengths $\bar{l}$, $\bar{l}_T$ and $\bar{l}_L$. Therefore, the results of numerical solution of equations (12)–(19) change. Namely, statistical weights $\rho(n, r, l)$ (equation (13)) and proportions of adjacent re-entry and random re-entry for $l_s > 0$ turn out to be quite different in comparison with those for $l_s = 0$. This will be demonstrated in the next section.

The thickness of the interfacial layer is a free parameter of the theory. We choose a value of l_s that eliminates any defects in local density within the amorphous region.

As our calculations show, the optimum value of thickness of this layer l_s is three CH_2 units. In this case, as shown in *Figures 2c* and *2g*, there is no excess density in the interfacial layer. Further increase in l_s results in a density deficiency in the interfacial layer (*Figures 2d* and *2h*).

RESULTS

In *Figure 3* the proportions of folds, loops and tie chains are presented as functions of the elongation of the macromolecule R/L and thickness of the amorphous region a.

Let us first describe the molecular morphology of the amorphous regions in isotropic polymers. For the amorphous region with $a = 100$ Å at $R/L = 0$ and $l_s = 0$ our calculations give the proportion of regular folds $v_{F'} = 7\%$, and the proportion of adjacent re-entrant loops $v_{A'} = 32\%$. As the thickness of the amorphous region decreases, $v_{F'}$ and $v_{A'}$ increase (*Figure 3b*, broken curves F′ and A′). *Figure 3* shows that in assuming the thickness of the interfacial layer to be $l_s = 3$ (in CH_2 units) the proportion of adjacent re-entry increases sharply at $R/L = 0$: from 32% at $l_s = 0$ to 78% at $l_s = 3$. The proportion of regular folds of length five CH_2 units grows from 7% to 38%.

As mentioned above, a consensus has been achieved as a result of earlier publications[7,9,17–21,23,24] in the discussion on the structure of the crystallite surface and interfacial layer. It was shown for different models that the degree of adjacent re-entry into crystallite v_A is equal to 74–80%. The value $v_A = 78\%$ obtained in the present publication using a different approach confirms this result.

Comparison of the broken curves F′, A′, L′ and the full curves F, A, L from *Figure 3* shows that the introduction of an interfacial layer of thickness $l_s = 3$ into

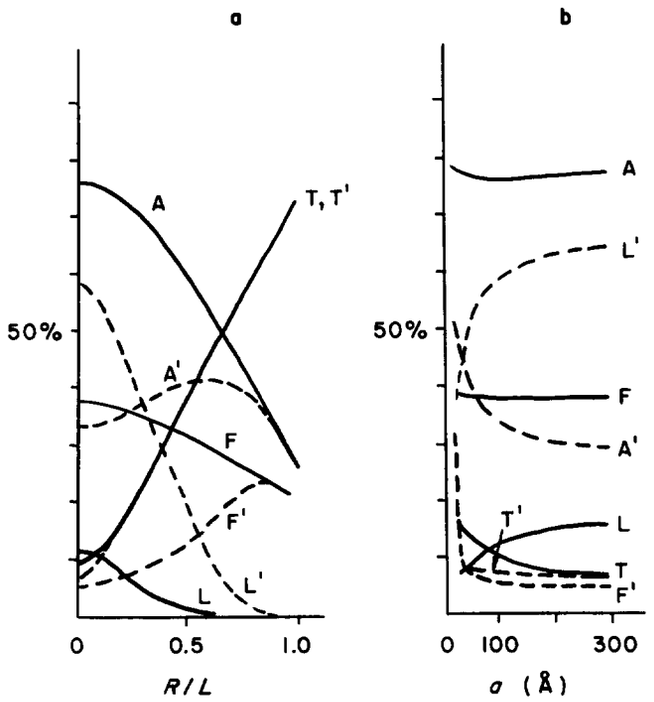

Figure 3 Dependences of portions of different types of subchains on R/L and a: (a) $a = 100$ Å, (b) $R/L = 0.01$; T,T', tie chains; L,L', random re-entrant loops; A,A', adjacent re-entrant loops; F,F', regular folds; $l_s = 0$ (A', F', L', T'), $l_s = 3$ (A, F, L, T); $d_a/d_c = 0.85$; temperature 360 K

the theory also results in a radical change in the dependences of the proportions of folds, and adjacent and random re-entrant loops on R/L and a. It should be remembered that the dependences represented by the broken curves F', A', L' correspond to an unrealistic situation of abnormally high local density in the vicinity of the crystallite surface. We present them only for a better understanding of the influence of the interfacial layer on the results.

On the contrary, introduction of the interfacial layer has a weak influence on the proportion of tie chains.

The proportion of tie chains at $a = 100$ Å and $R/L = 0$ equals $v_T = 10\%$. It is nearly three times as big as that in the gambler's ruin problem (3% at $a = 100$ Å). This proportion grows more slowly with decreasing a than in the gambler's ruin problem (*Figure 2b*, curves T, T').

As macromolecule elongation R/L increases due to polymer drawing, the proportion of tie chains increases (at $R/L > 0.2$ nearly linearly – *Figure 3a*, curve T). The analysis of numerical data shows that, at such values of R/L, $v_3 \gg v_4$ and the proportion of tie chains:

$$v_T \simeq v_3 \simeq \frac{R}{L}\frac{c + (d_a/d_c)a}{c + a} \qquad (28)$$

This result is in good agreement with the experimentally known nearly linear dependence of polymer strength on drawing ratio[4,5].

Figure 3b demonstrates a weak dependence of any subchain proportion (F, A, L, T) on the thickness of the amorphous region a at $R/L = 0$. It is worth mentioning that at $R/L > 0.2$ these proportions do not practically depend on a at all.

Our calculations have been carried out for two values of density of the amorphous layer: $d_a/d_c = 0.85$ and $d_a/d_c = 1$. The influence of this ratio on the results is small up to $R/L = 0.8$. At $R/L > 0.8$ and $d_a/d_c = 0.85$, no value of β exists which would satisfy equation (12). At $d_a/d_c = 1$ such a value of β exists up to $R/L = 1$. Thus the model indirectly predicts an increase in the amorphous region density with increase of drawing ratio. This agrees with experiment[1,2].

As distinct from other publications[25,26] our model does not predict a pronounced relationship between the parameters of molecular morphology of the amorphous region and crystallite thickness c and temperature T. Formula (25) gives some idea about the effect of the value of c on the results. The degree of temperature influence is seen from *Figure 4*. This figure demonstrates the form of the length distributions of tie chains and loops and their dependence on the ratio R/L.

Figure 5 shows the average length of tie chains and loops (including regular folds) as a function of a for various values of R/L. For tie chains all the given

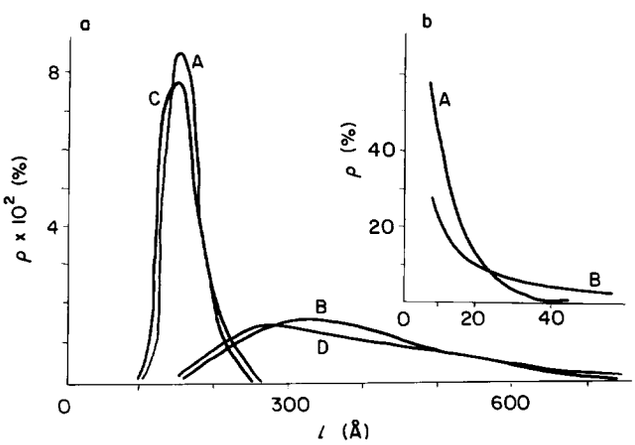

Figure 4 Length distributions of (a) tie chains and (b) loops (including regular folds): $a = 100$ Å; $d_a/d_c = 0.85$; curve A, $R/L = 0.4$, $T = 273$ K; curve B, $R/L = 0$, $T = 273$ K; curve C, $R/L = 0.4$, $T = 413$ K; curve D, $R/L = 0$, $T = 413$ K

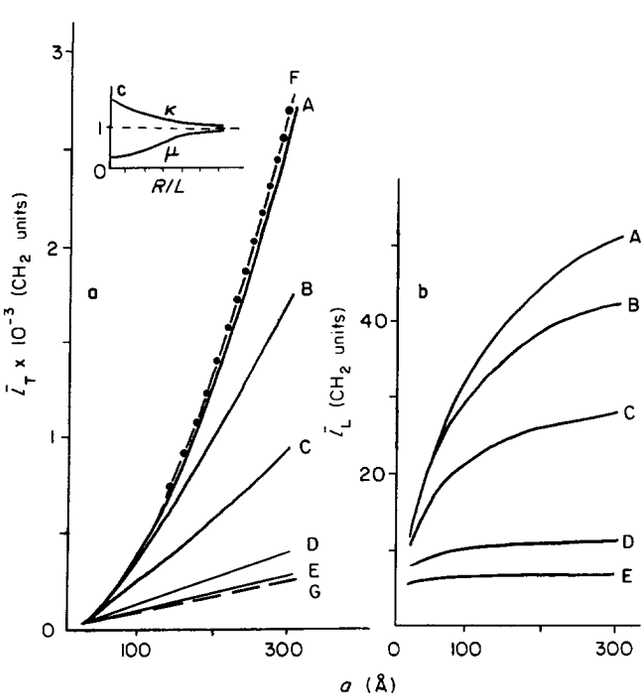

Figure 5 Dependences of average lengths of subchains on a at various R/L: (a) tie chains, (b) loops (including regular folds); $R/L = 0$ (A, F), 0.1 (B), 0.2 (C), 0.5 (D), 0.8 (E), 0.9 (G); $d_a/d_c = 0.85$ (A–E), 1 (F, G); temperature = 360 K. (c) Dependences of parameters μ and κ on R/L (see formula (26))

relationships (*Figure 5a*) can be approximated with sufficient accuracy by the formula:

$$l_T = \mu a^{\kappa} \quad (29)$$

Coefficients μ and κ depend on the ratio R/L (*Figure 5c*). At $R/L = 0$, index κ equals 1.7. In the gambler's ruin model the average length of tie chains is proportional to a^2. Thus, at the same value of a our theory predicts a smaller value of the average tie chain length than does the gambler's ruin model. For instance, at $a = 100$ Å, l_T is twice as small in our theory as that in the gambler's ruin model.

The mean-square deviation for tie chains Δl decreases rapidly as R/L increases. According to the experimental data[2,32], Δl for highly drawn polymers is less than 10% of the amorphous region thickness. Our theory predicts such values of Δl at $R/L > 0.8$.

The average length of loops $\bar{l}_F$ decreases and the dependence of $\bar{l}_F$ on a disappears as R/L increases. At $R/L > 0.5$, $\bar{l}_F$ is less than twice as long as the regular fold.

DISCUSSION

Until recently the most detailed information about molecular morphology of the amorphous region of semicrystalline polymers was provided by the gambler's ruin model. The theory presented here has a quite different foundation and provides at least as detailed information as the gambler's ruin model for both isotropic and drawn polymers. The predictions of these theories concerning the proportions of adjacent re-entrant loops and regular folds are quite similar. There is qualitative agreement with respect to the dependences of the proportions of tie chains and loops and their average lengths on the amorphous region thickness a, but there is no quantitative agreement. Our theory predicts that the proportion of tie chains is considerably greater and its dependence on a is considerably weaker than in the gambler's ruin problem. The average length of tie chains at $a = 100$ Å is twice as small as that in the gambler's ruin problem and is affected by a considerably more weakly.

The anisotropic variant of the gambler's ruin model (see formulae (A11a), (A12a), (A20) and (A21) of ref. 9 and ref. 33) predicts independence of the proportions of different types of subchains on the degree of chain extension if the anisotropy is strong enough. The same is predicted by our theory. However, the proportions of different types of subchains and their length distributions predicted by our theory differs quantitatively as compared with the anisotropic gambler's ruin model predictions.

In this paper the proportions of loops and tie chains are considered to be affected by the molecular parameter R/L. To consider the dependence of these proportions on macroscopic draw ratio λ, the well known relation:

$$\lambda = (R/L)(N/C_N)^{1/2} \sin\theta - 1 \quad (30)$$

should be used, where N is the number of CH_2 units in the chain, θ is the bond angle and C_N is a characteristic ratio for the chain with N units. So far, by L we have meant the contour length of the entire macromolecule, and by R its end-to-end distance. However, in reality, macromolecules form an entanglement network. If the network is sufficiently loose (and N is sufficiently large), we can refer L and R to a polymer segment located between two crosslinks of the network. If, however, the polymer segments of the network are comparable with the size of crystallites c, this cannot be done, since our theory requires that L be much longer than c. However, taking into account the fact that in the draw process reptations and disentanglements are inevitable, the value of the polymer segment in the network is unlikely to be considered as a well determined parameter, and additional investigation is required in this field.

There is a good deal of experimental data[1,2] indicating that the structure of a polymer (in particular the proportion of loops and tie chains) depends on the kinetics of crystallization and drawing. One should not consider that our theory is at variance with these facts. According to the theory, the molecular morphology of the amorphous region corresponds to a minimum of the free conformational energy *under the given limitations* (c, a, R/L are considered to be constants), i.e. it corresponds to a *local* thermodynamic equilibrium. The limitations mentioned above are assumed to reflect the kinetics of the crystallization and drawing.

CONCLUSION

The theory affords a solution to the problem of the molecular morphology of the amorphous region in both isotropic and highly drawn polymers. It is based on the assumption that molecular morphology corresponds to a minimum of the total free conformational energy of subchains in amorphous regions provided that the thicknesses of crystallites c and amorphous regions a, the degree of macromolecule extension R/L and the ratio of densities d_a/d_c are given parameters.

Detailed information about the dependences of the proportions of tie chains, loops and folds on a and R/L is obtained. These dependences are qualitatively similar to those of the gambler's ruin model (in its isotropic and anisotropic variants), though considerable quantitative differences are seen.

Monte-Carlo calculation of the local density distribution within the amorphous region was carried out. It was shown that an interfacial layer between the crystallite and the amorphous region should be introduced into the theory to avoid a density excess in the vicinity of the crystallite surface. Within the interfacial layer the conformations of long subchains are limited. The optimum thickness of the interfacial layer was found to be equal to three CH_2 units. The introduction of this interfacial layer considerably affects the proportions of adjacent and random re-entrant loops and their dependences on a and R/L.

The value obtained in the theory for the proportion of adjacent re-entry (78%) confirms the consensus reached in this field.

The predictions of a linear dependence of the proportion of tie chains on the degree of macromolecule extension R/L and values of the mean-square deviation of the tie chain distribution at high values of R/L correspond satisfactorily to the available experimental data.

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